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EVALUATION OF SAMPLING METHODS FOR GASEOUS ATMOSPHERIC SAMPLES

by

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A research program was conducted to test and evaluate several alternatives for collecting and transferring samples from the collection site to the laboratory for the analysis of a variety of toxic organic pollutants by gas chromatography (GC). Sample storage media included three types of polymeric bags (FEP® Teflon®, Tedlar, five-layered aluminized bags), glass bulbs, electropolished and Summa® polished cannisters, Tenax® GC and charcoal cartridges, and nickel cryogenic traps. Twenty-seven test compounds including hydrocarbons, aromatics, halogenated hydrocarbons, halogenated aromatics, and oxygen, nitrogen and sulfur-containing compounds were used to test the storage media. Dynamically flowing mixtures of these gases were synthesized using a specially designed permeation/dilution system. Quantitative laboratory stability tests were conducted with Tenax® GC, charcoal, and cryogenic traps at 2 concentration levels of 50 parts per billion (ppb) and 200 parts per trillion (ppt), for 15 of the 27 chemicals. Quantitative stability tests were conducted with the remaining storage media at one concentration level, nominally 50 ppb, for the same 15 chemicals. The stability tests were conducted over a 7 day storage period. The potential effect of inorganic gases as interferences during the collection of test compounds was quantitatively studied. An automatic two channel ambient air sampler utilizing sorbent cartridges as the collection medium was also designed and fabricated. A quality control and quality assurance (QC/QA) program was extablished and maintained for all measured and analyzed data.

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ABSTRACT

A research program was conducted to test and evaluate several alternatives for collecting and transferring samples from the collection site to the laboratory for the analysis of a variety of toxic organic pollutants by gas chromatography (GC). Sample storage media included three types of polymeric bags (FEP Teflon®, Tedlar, five-layered aluminized bags), glass bulbs, electropolished and Summa® polished cannisters, Tenax® GC and charcoal cartridges, and nickel cryogenic traps. Twenty-seven test compounds including hydrocarbons, aromatics, halogenated hydrocarbons, halogenated aromatics, and oxygen, nitrogen and sulfur-containing compounds were used to test the storage media. Dynamically flowing mixtures of these gases were synthesized using a specially designed permeation/dilution system. Quantitative laboratory stability tests were conducted with Tenax® GC, charcoal, and cryogenic traps at 2 concentration levels of 50 parts per billion (ppb) and 200 parts per trillion (ppt), for 15 of the 27 chemicals. Quantitative stability tests were conducted with the remaining storage media at one concentration level, nominally 50 ppb, for the same 15 chemicals. The stability tests were conducted over a 7 day storage period. Also, quantitative stability tests were conducted with Summa® polished cans, glass bulbs, Tedlar® bags and Tenax® GC cartridges at one concentration level, nominally 50 ppb, for the remaining group of chemicals.

The potential effect of inorganic gases as interferences during the collection of test compounds was quantitatively studied with Tenax® GC, charcoal, cryogenic traps, Summa® polished cans, glass bulbs and Tedlar bags at two concentration levels of inorganic substances for approximately one-half of the test compounds. The remaining test compounds were also collected in the presence of inorganic gases using Tenax® GC cartridges, Summa® polished cans, glass bulbs and Tedlar bags.

Sampling systems were designed and fabricated as necessary to collect valid gas samples for the quantitative tests conducted with the various

collection devices using a permeation/dilution system for the synthesis of a dynamic flow, synthetic air vapor mixture.

A quality control and quality assurance (QC/QA) program was established and maintained for all measured and analyzed data. This QC/QA program included the following elements: (a) sampling procedures; (b) calibration procedures; (c) analytical procedures; (d) data collection and reporting procedures; (e) auditing procedures; (f) storage procedures; and (g) computational and data validation procedures.

The sample collection and transfer methods were tested, evaluated and compared for the following elements: (a) limits of applicability; (b) collection and recovery efficiency for gas chromatographic analysis; (c) analytical accuracy and detection limits; (d) interferences by inorganic gases; (e) sample stability in storage; (f) quality of chromatograms; and (g) simplicity and convenience. Because of resource limitations, however, statistical analyses of data on comparing methods by chemical or group types and on interference effects were not conducted.

The support coated open tubular (SCOT) capillaries coated with SE-30 were the best available when this research was initiated and performed adequately throughout the study. They were rugged with two SCOTs per instrument required over a three year usage. Fused silica capillaries were not commercially available when the program started and, thus, there was no opportunity to evaluate them.

An automatic two channel ambient air sampler utilizing sorbent cartridges as the collection medium was designed and fabricated. The mechanical and electronic systems of the automatic sampler were designed and built from commercially available components to include the following features: (1) two sampling channels with two sampling heads with provisions for six samples per head and a blank, (2) capability for collecting 12 single or 6 duplicate samples, (3) variable orifices, which are manually set for low flow rate settings and range through each channel, (4) sampling rates settable from 7 mL/min to 1.5 L/min, (5) a mass digital flow meter (switchable to each channel individually, or measurement of total flow for both channels) with the ability to integrate total flow, (6) solid-state timer system with clock integrator, printer and manual mode, (7) sampling periods selectable at 15, 30, 45 and 60 min, and 0.5, 2, 3, 6, 8 and 12 hr, (8) reset capability for flow integrator after collection of each sample (but not after a power failure), and (9) operative on 120V alternating current.

The automatic sampler's systems were checked to insure proper electrical and mechanical functioning under laboratory simulated conditions. These tests included stepping sequences, clocking, printing, resetting, and sampling head sealing (pressure). Calibration of functions such as flow meter, integrator, timers, etc. was conducted. Background tests on sorbent cartridges sealed in sampling heads were also instituted.

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SECTION 1

INTRODUCTION

The chemical characterization of atmospheric pollutants is of major importance in determining primary sources, elucidating chemical transformation pathways in the atmosphere and determining their potential risk to the environment and the populace. Since chemical compounds present in the atmosphere include both vapor phase organics (1) and particulate organic matter (2), it is important that collection and analytical techniques encompass the entire spectrum of substances.

Air pollutants are classified as primary or secondary. Primary atmospheric pollutants are natural (e.g. dust, vegetation, etc.) or anthropogenic in origin (e.g. smoke stack and vehicular emissions 1-3). Secondary products are generated from primary pollutants, i.e. via atmospheric (photochemical) reactions.

The amount of vapor phase organics emitted anthropogenically in the United States has been estimated at 1.9 x 10^{13} g/year. World wide emission has been estimated to be about 7.5 x 10^{13} g/year. The levels of vapor-phase organics are generally 10-50 times greater than particulate organics (4).

Most atmospheric pollutant samples are extremely complex in nature containing perhaps hundreds of different molecular species with a very large dynamic range of concentration. This complexity may necessitate the use of high resolution techniques such as capillary column gas chromatography and/or high performance liquid chromatography. Pre-separation techniques may be required and also methods which provide for definitive chemical analysis of samples such as mass spectrometry (5-12).

The successful chemical analysis of the vapor phase organics depends upon a number of important steps beginning with the collection and/or preconcentration techniques. During the past decade significant advances have been made in the development of collection methods for vapor-phase organic materials in the atmosphere. Collection methods now available include those techniques which trap organic vapors on sorbent surfaces (6-13), condense/freeze vapors in cryogenic traps (14,15) or confine the pollutants in evacuated stainless steel cannisters or bags (16,17).

One of the major problems encountered in sampling vapor-phase organics is the presence of water. The relative abundance of water in the atmosphere is high (often greater than 10^4 fold) compared to that of organic species of interest and many of the collection and analysis methods (such as gas chromatography columns) do not tolerate large quantities of water. Simultaneous concentration of water with organic material causes partial dilution of the samples thus impeding sensitive analysis of the vapor-phase organics. Sample volatility also limits the ability to concentrate analytes in subsequent steps.

Several primary criteria for evaluation of collection devices for air sampling of vapor-phase organics have emerged from previous studies: (a) ability to discriminate against water and preferentially concentrate the vapor-phase organics of interest; (b) low background contribution from the sampling media during subsequent analysis; (c) minimal decomposition or polymerization of the sampled constituents during collection and recovery; (d) quantitative collection efficiency and recovery of trapped or confined vapors; (e) high breakthrough volumes for sorbent-based collection devices, and (f) collection systems that do not contribute to in situ formation of artifacts (5-13).

Although a number of collection devices have been reported and applied by researchers, there are no reports in which a comparison has been made of the various collection devices. The strengths and weaknesses of each of the collection devices (containers and traps) have not been evaluated in a concerted and thorough fashion in terms of the primary criteria outlined above. None of the methods which are currently in use for collecting gaseous atmospheric samples have been shown to be completely satisfactory for all chemical species at all concentrations. Limits of applicability are not well-defined and is the subject of this research report. Plastic bags outgas residues from the plastic film and are subject to diffusion through the bag walls. Certain chemicals species may be adsorbed on the walls of glass or stainless steel containers or undergo reactions at active sites on the walls. However, these factors have not been thoroughly compared among the various collection devices. Concentrating gaseous samples in cold traps is a cumbersome procedure and is not well suited for field sampling by unskilled personnel at the present time. The relative high concentrations of water in the atmosphere may plug the trap, interact with certain pollutants causing artifacts or interfere with subsequent analysis. Traps packed with adsorbent materials and operated at ambient temperature do not efficiently collect the more volatile pollutants and the strongly adsorbed pollutants may be difficult to remove from the adsorbent trap. Long term storage of gases in any case may result in losses of pollutants through diffusion or slow reactions from other chemical species or with materials of the container.

When this research program was initiated, a sampling system for sorbent cartridges capable of collecting several sequential replicate or single samples (unattended) was not commercially available. The need for an automatic sampler which could collect organic vapors from ambient air over a prescribed flow range (e.g. 5 mL/min to 1.5L/min) and sampling period intervals (e.g. 15 min to 24 hr) precipitated a design and fabrication effort.

The U.S. Environmental Protection Agency has been concerned with these analytical problems and a program to test and evaluate various methods of collecting and analyzing gaseous atmospheric samples for a variety of toxic organic pollutants by gas chromatography was performed and is reported here. By defining the limitations and applicability of the techniques, a more comprehensive approach to the analysis of organic pollutants may be formulated for future studies.

SECTION 2

CONCLUSIONS

Three type of polymeric bags (FEP Teflon®, Tedlar, and five-layer polyethylene-aluminized), glass bulbs, stainless steel cannisters (electro and Summa®-polished), and Tenax® GC, charcoal and nickel cryogenic traps were evaluated for: (1) simplicity and convenience; (2) collection and recovery efficiency for GC analysis; (3) accuracy, reproducibility and limits of detection; (4) analyte storage stability; (5) potential interferences from inorganic gases [ozone, NO_x, SO_2] and water, and (6) limits of applicability [chemical/physical properties of chemicals, background, field conditions]. Because of a limitation in resources a rigorous statistical evaluation of data addressing these six issues could not be conducted, and thus, in many cases only qualitative trends can be described.

In order to test the various collection methods, a permeation/dilution system was designed and fabricated for this research program. The general difficulty in the use of this system was attributed to potential adsorptive losses of the chemicals of interest at highly dilute levels. Adsorption studies were conducted with radioactive dimethylamine, hexadecane, and bromobenzene. Adsorptive losses were essentially 100% for dimethylamine at the low ppb level while recoveries were 88-90% for bromobenzene. Attempts to deactivate the glass surfaces in the system with silanizing agents and a Carbowax 20M treatment were not successful as tested by the transmission of dimethylamine. Approximately 40-50% of the radioactive hexadecane passed through the system when the system was maintained at 150°C. Thus, chemicals with boiling points higher than bromobenzene would require higher temperatures to minimize adsorptive/condensation losses to the surface of the system. The system was operated at 200°C.

Commercial sources of reference standard or NBS certified synthetic air/vapor mixtures were not available for most of the chemicals when this program was initiated. None of the sources of chemicals used here for the preparation of a dynamic flowing synthetic air/vapor mixture were traceable to a reference standard. As such, all synthetic air/vapor mixtures were synthesized utilizing a permeation tube concept. The permeation tubes for many of the 27 test compounds exhibited permeation rates within ±10% (RSD) over a several month period. Permeation tubes of chloroprene, 1,2-dichloropropane, 1,1,2,2-tetrachloroethane, α-epichlorohydrin, and nitrobenzene exhibited permeation rates with variability >±10%. Thus in the evaluation of the collection methods, the uncertainties associated with the absolute accuracy and reproducibility should be noted in drawing conclusions from the reported data.

Although bags have the advantage of allowing 10-100 L of samples to be collected for replicate measurements, they are easily punctured and clear bags must be protected from light after sample collection. Thorough cleaning to remove volatile organic background can be complicated since the bags cannot be heated excessively without the seams developing leaks. Cleaning with ozone and ultraviolet light was necessary to reduce levels of high boiling contaminants in Teflon® and Tedlar bags. The background level in the five-layered polyethylene-aluminized bags was so severe and unacceptable after attempted cleaning, that they were deemed unsatisfactory for environmental sampling and were not further evaluated in this program.

Recoveries for 15 test compounds collected from a dynamic flowing synthetic air/vapor mixture for Teflon® and Tedlar bags were generally in the range of 70-100%. The highest recoveries were found for the most volatile chemicals in the synthetic air/vapor mixture while recoveries decreased with the less volatile substances. However, with time the decrease in recovery was generally more rapid with Teflon® than with Tedlar bags. Both types of bags exhibited both loss of compound and influx of contaminants by permeation through the bag walls. Teflon® and Tedlar bags should be stored in clean environments or should be analyzed within 4 h after sample collection.

The potential interferences from inorganic gases present during the sampling of test compounds decreased the recovery of most test compounds from Tedlar® bags. One adverse effect caused by the presence of inorganic gases was the release of unknown contaminants from the wall of the Tedlar® bags which appeared as background during analysis.

The amount of sample collectable in a glass bulb is limited with usually 1-2 L available for analysis. Glass bulbs were easily broken especially during the filling step of the bulb. Bulbs should also be protected from light after sample collection. Bulbs must be cleaned and this can be facilitated by heating while evacuating which improves efficiency of the cleaning process though care should be taken not to heat the stopcock valves employed. Cleaning with a solution was difficult and time consuming since the valves must be disassembled and this operation leads to a high incidence of breakage.

The recovery of test compounds from glass bulbs decreased rapidly with increased boiling point and was above 90% for only a few test compounds. The sampling of test compounds in the presence of potential interferences from inorganic gases generally decreased their recoveries over those obtained with low level interferences.

As with glass bulbs, steel containers allow recovery of only limited sample volume, typically 4-6 liters. They are however extremely rugged and could be cleaned thoroughly by heating while evacuating. The Summa® polished containers generally show higher recoveries for high boiling compounds than electropolished containers. Also the Summa® polished containers exhibited a better maintenance of recovery with time than the electropolished containers. Sampling in the presence of high level of inorganic gases as potential interferences decreased recoveries for some compounds and increased them for others. These increases may be due to further displacement by water of the test compounds and/or release of contaminants not released during cleaning.

The NIOSH charcoal cartridges evaluated in this program were found to be generally inadequate as applied to the sampling of environmental levels (low ppb) of test compounds. The limits of applicability of charcoal cartridges are revealed in the overall poor recovery of organics. For the analysis of test compounds, GC/FID and GC/ECD were employed and only when using GC/ECD were the limits of detection adequate for some of the chemicals of interest. None of the test compounds collected in the low ppb range and a 30 L sample volume were detected by GC/FID. The recovery of chemicals measurable by ECD was poor and the precision was erratic which prohibited the establishment of storage characteristics.

Initial storage-stability studies with nickel cryogenic traps (as prescribed by EPA) cooled with dry ice yielded poor recoveries for all chemicals at the low ppb level (1 L/min sampling rate). The cryogenic traps were then modified by filling with clean glass beads and liquid oxygen was used as the cryogen. Most of the compounds were detected but the absolute recoveries were still low and the precision was poor. The applicability of cryogenic traps of the design evaluated in this study was limited. This method was labor intensive during sample collection, sample transfer and storage, and sample recovery and analysis. Cryogenic traps were the least convenient of the collection methods described.

The Tenax® GC sampling cartridge was limited principally in the breakthrough volume which directly determined the detection limits obtainable for given measurement techniques. In this study a 30 L sampling volume was employed and thus the breakthrough volumes for chemicals that are less than the sampling volume will severely limit their detection and quantification. Similarly, the collection efficiency was directly related to the breakthrough volume. Recoveries of chemicals were not significantly decreased by short-term storage (7 da). The precision of recoveries was slightly less than those observed for containers; however, with Tenax GC cartridges, the recovery was based upon triplicate sample analysis and not measurement of the same sample. A major attribute of a cartridge sampling concept is its simplicity and convenience in its preparation, sample transport, and recovery and analysis. It is one of the few techniques which is amenable to personnel sampling. Large numbers of samples can be taken simultaneously, stored until analysis and analyzed relatively rapidly.

Experiments with potential inorganic gas interferences demonstrated a major problem which can occur with any collection device. Reactive inorganic gases in the atmosphere can perturb the quantitative and qualitative composition of the air sample (parent compounds disappearing and new artifacts appearing) during collection of organics. Substantial improvement without absorptive loses was obtained by using a very small amount of mild reducing agent to remove ozone prior to trapping, *i.e.*, Tenax® GC sampling.

The following table exhibits the relative performance of the collection devices for the sampling of synthetic air vapor mixtures with and without the presence of inorganic gases in the parts-per-billion levels of test organic compounds:

Collection Method (No. Compounds Tested)	No. of Compounds in Recovery Range				
	>95%	90-95%	80-90%	70-80%	60-70%
Teflon® (15)*	4	0	2	5	1
Tedlar (27)*	5	1	6	6	3
Tedlar (27)**	2	1	10	3	2
Glass bulbs (27)*	4	2	2	5	6
Glass bulbs (27)**	2	3	5	5	2
Summa® polished SS cannister (27)*	10	5	2	3	1
Summa® polished SS cannister (27)**	4	1	4	4	2
Tenax® GC cartridge (27)*	12	3	4	0	2
Tenax® GC cartridge (27)**	11	3	0	2	0

*ppb levels of test compounds sampled and then analysis immediately conducted.

**ppb levels of test compounds in the presence of low levels of inorganic gases sampled and then analysis immediately conducted.

The two sampling techniques which show the greatest promise under all of the laboratory tests conducted are the Summa® polished stainless steel cannisters and the Tenax® GC sampling cartridge. The Summa® polished cannister gave the highest recoveries for the more volatile chemicals in the test group, while the Tenax® GC sampling cartridge performed better for those chemicals with breakthrough volumes larger than the sampling volumes. Thus, these two collection techniques can compliment each other when sampling a broad spectrum of vapor-phase organics in the atmosphere is desired.

Support coated open tubular (SCOT) capillaries were employed for resolving the test compounds. The stationary phase was SE-30. The SCOT capillaries performed adequately in these studies. After much of the research on this program had been performed with SCOTs, fused silica capillaries became commercially available; however, these was no opportunity to evaluate their performance.

The performance of a newly designed and built automatic sampler was laboratory tested. Both in the parallel and serial modes (1 to 6 channels in duplicate and 1 to 12 channels, singly) the stepping sequencer was found to step through each channel in the proper order. Also, the sampler was tested for sampling periods at 15, 30, 45 and 60 min, and 2, 12 and 24 hr and was found to step through the channels correctly at the proper time intervals.

The sampler's digital flow meter was calibrated to read the actual flow rate being sampled by adjusting zero and gain controls. The sampler set and actual flows (0.19% relative standard deviation, N = 6) agreed within 2% in the parallel and serial modes. Initial evaluation of the printout from the integrator (total volume) and its agreement with the actual volume sampled revealed a 20% and 3-5% deviations in the serial and parallel modes, respectively. After calibrating the integrator both modes were within 5%. No significant drift was detected between the digital flow meter/integrator registered volume and actual volume over 24 hr of operation.

Various sealing designs (phenolic screw cap and bolt-type arrangement with Teflon or Viton o-rings) in the sampling heads were tested and the bolt-type was superior. No leaks were found at 10 psi of helium when Viton o-rings were used. Tenax® GC sampling cartridges stored in bolted end plate sampling heads exhibited background levels typical of cartridges stored in culture tubes.

SECTION 3

RECOMMENDATION

Upon conducting a number of laboratory tests using test compounds and synthetic air vapor mixtures, a few collection devices have been found to be sufficiently accurate with synthetic mixtures to be further tested with atmospheric samples. The recommendations offered here specifically address the further testing of Tenax® GC sampling cartridges, "Summa" polished cans and glass bulbs. Field studies should include at a minimum three industrial sites and one rural area for the additional testing of these three collection devices. It is recommended that field testing protocols be developed prior to the collection of field data and that these protocols incorporate the following elements:

(1) the use of 20 or more deuterated surrogate test compounds selected from those previously studied in laboratory experiments for the evaluation of the collection devices;

(2) quantitative and qualitative analysis using capillary gas chromatography/mass spectrometry;

(3) collection of triplicate samples at each field site;

(4) collection of a set of both day and night samples;

(5) the incorporation of quality control procedures, *e.g.*, blanks, etc.

(6) determination of potential interferences of each test compounds where possible, and

(7) calculation of accuracy and precision of collection and analysis methods.

The use of deuterated surrogate compounds allows for the distinction between endogenous and exogenous pollutants when mass spectrometry is used as the measurement technique, as well as the differentiation between endogenous and artifactually formed compounds. Thus, by spiking the atmospheric samples in a continuous fashion with deuterated compounds, the true collection accuracy can be assessed as well as the reproducibility of analysis. The absolute and relative recovery should be determined by the use of internal standards.

It is recommended that the development and employment of quality control and assurance practices be established in developing quality data and to ensure the validity of the results obtained from the field evaluation for these three collection devices. These quality control and assurance practices should include at a minimum the following:

(1) gravimetric calibration of permeation tubes and statistical analysis of permeation rates;

(2) GC/MS instrument calibration checks [e.g. instrument performance and chromatography column performance], and

(3) flow calibration of pump systems used in the field studies.

In addition to the field testing of these three collection devices further research is recommended regarding the automatic sampler. These recommendations are in (1) design refinements and (2) the field evaluation.

Recommended design refinements include:

(1) removing the pump from the control console with a quick connect coupling to the console making the console smaller, lighter and cooler;

(2) placing the calibration port in front of the variable orifice valves (i.e. parallel to the inlet-ports) so that the flow rate through each channel can be set easier prior to the beginning of a run, and

(3) the provision of external battery jacks on the front panel. A feature for providing power to the timing circuitry for cases where line power outages occur and print-out of the information in the recording registry can be made.

Further laboratory and field testing of the automatic sampler should include:

(1) determining the accuracy and reproducibility of sampling synthetic air/vapor mixtures from a permeation dilution system as described in this report (with the variables of sampling time and rate evaluated);

(2) long-term storage (months) of clean Tenax® GC cartridges in sampling heads to determine the background which may occur;

(3) the effect of transportation on background of the blank Tenax cartridge in the sampling head.

(4) determine accuracy and reproducibility under atmospheric (field) sampling conditions to include (a) sampling in light and heavy particulate loads, (b) a comparison of Teflon® _vs_. glass fiber filter, (c) sampling times and rates, and (d) sampling under heavy and light vapor-phase pollutant loads.

(5) determine its reliability under (a) extreme weather elements such as temperature and humidity, and (b) power transcient effects occurring during stormy weather and recovery of the sampling system, and

(6) evaluate the automatic sampler using deuterated surrogate standards in a field sampling protocol design as developed for the Tenax® GC sampling cartridge described above.

SECTION 4

PROGRAM OBJECTIVES

The primary objective of the research project has been the comprehensive evaluation and testing of six collection devices and the particular analytical procedures associated with each of these devices. The component objectives of this study have included: (1) the preparation of a comprehensive program design for the evaluation and testing of the six devices (polymeric bags, glass bulbs, metal containers, Tenax and charcoal absorbent traps, and Ni cryogenic traps); (2) the selection of model compounds for systems evaluation; (3) the preparation and calibration of permeation tubes; (4) the design and performance testing of a portable permeation system; (5) the delineation of sampling and analysis procedures; and (6) the design and fabrication of an automatic sampler.

Although not a specific initial objective of this program, some experiments on optimization of collection devices (*e.g.* polymeric bags, glass bulbs, and nickel cryogenic traps) were needed and conducted as required by a subsequent technical directive. Also, design changes of the automatic sampler were instituted as specified in a technical directive.

COLLECTION DEVICE EVALUATION

As stated, the primary objective of this research project has been the evaluation of six gas collection devices. The elements of the evaluation included determination of the following:

(1) limits of applicability;
(2) collection efficiency;
(3) recovery (transfer) efficiency for gas chromatographic analysis;
(4) analytical accuracy and detection limits;
(5) effect of potential interferences (including ozone, SO_2, NO_x, and water vapor);

(6) sample stability and storage;

(7) quality of chromatograms;

(8) simplicity and convenience of the sample collection and transfer methods.

The objective included not only evaluation of each of these elements for each collection device but also a comparison of the evaluation results obtained with each device so that the overall "best" devices might be selected for field testing in a future project.

The evaluation was to be performed using a variety of test conditions. Mixtures of test compounds were to be collected under various conditions. Using these compounds, the test parameter relationship for the collection and storage experiments to be used are given in Table 1.

In experimental design (A) the sampling volume and the relative humidity (30%) were to be held constant. No potentially interfering substances (O_3, SO_2, NO_x) were to be added. The variable parameter was to be the concentration of each individual substance and storage time. In this case, the concentrations were to be zero, [illegible] less than 10 ppt (low) and not more than 100 ppb (high). In the second experimental design (B), the ozone, SO_2, and NO_x concentrations, and relative humidity were to be varied while the sampling volume, time and rate, and concentrations were to be constant. All sampling devices were to be evaluated simultaneously by sampling the test atmosphere at the same time to reduce possible variability in the performance of the permeation system.

SELECTION OF MODEL COMPOUNDS

The experimental design incorporated an approach which provided for a quantitative comparison of the various sampling methods. A set of 27 test compounds was selected for this study and it is given in Table 2. The initial criterion for selection of test compounds was based upon the production level in the U.S. and their toxicity data. These data are incorporated as provided by the U.S. EPA.

For each chemical group, several compounds were included to provide a range of chemical and physical properties which would reveal the strengths and weaknesses of the collection devices. For chloroalkanes, methyl chloride represented the most volatile organic (b.p. -24.2°C) and 1,1,2,2-tetrachloroethane (b.p. 146.2) as the least volatile (Table 2). In addition to a wide

Table 1. TEST PARAMETER RELATIONSHIPS FOR EVALUATION OF COLLECTION DEVICES

Experimental Design	Test Parameters	Constant Parameters
A	Concentration (Two levels > 10 ppt < 1 ppb and > 1 ppb < 100 ppb)	Volume, sampling time and rate RH = 30%
		$[O_3] = 0$ $[SO_2] = 0$
		$[NO_x] = 0$
	Storage Time (0, 3, 7 da)	
B		Test mixture concentration
	$O_3/NO_x/SO_2$	Volume, sampling time and rate
	Relative humidity	

Table 2. TEST COMPOUNDS SELECTED FOR USE IN QUANTITATIVE EVALUATION STUDIES OF SAMPLE COLLECTION METHODS

Chemical Group	Compound	B.P. (°C)	Estimated U.S.[a] Production (10^6 lb/yr)	Toxicity[a]		
				Carcinogenicity	Mutagenicity	Acute
Chloroalkanes	Methyl chloride	-24.2	460	-	+	H
	1,2-Dichloropropane	96.4	(30)			H
	Chloroform	61.7	260	+	-	H
	1,1,2,2-Tetrachloroethane	146.2	-	+	+	H
	1,1,1-Trichloroethane	74.1	75	-	-	M
Chloroalkenes	Vinyl chloride	-13	4180	+	weak +	H
	Tetrachloroethylene	121	680-1210	±	-	M
	2-Chloro-1,3-butadiene	59.4	349	+	+	H
	1,1-Dichloroethylene	37	260	±	+	L
	Allyl chloride	45	290	±	+	H
Chlorinated aromatics	Chlorobenzene	132	690			M
	m-Dichlorobenzene	173	-			
	Benzyl chloride	215	80	+	+	H
Aromatics	Benzene	80.1	1400	±	+	H
	Toluene	110.6	6940	-	-	M
	1,2,3-Trimethylbenzene	176.1	-			
	Ethylbenzene	136.2	-			
	o-Xylene	139.1	1000	-	-	M
Alkanes	n-Decane	174.1	-	+		L
Nitro compounds	Nitrobenzene	210.8	550	-	-	H
Phenols	o-Cresol	190.9	(30)	Promoter (?)		M
Acrylo compounds	Acrylonitrile	77	1410	+	+	H
Ethers	Furan	31.4	-			H
	Bis-(2-chloroethyl)ether	178	1 (?)	±	+	H
	Propylene oxide	34.3	-	-	+	M
	α-Epichlorohydrin	116.5	500	+	+	H
Sulfur compound	Methyl mercaptan	6.2	-			M

[a] Quantities in brackets are estimated from reported production of mixtures containing the compound. Symbols (+ and -) indicate test results, ± indicates uncertainty. Data provided by EPA.

range in boiling points, other compounds were selected for their unique chemical reactivity. For example, 1,1,1-trichloroethane under certain catalytic conditions will decompose to vinylidene chloride.

Among the chloroalkenes (Table 2), the volatility range was -13°C (vinyl chloride) to 121°C (tetrachloroethylene). 2-Chloro-1,3-butadiene (chloroprene), an isomer of vinyl chloride ("1-vinyl vinyl chloride"), is highly reactive toward self-polymerization and destruction by ozone. Allyl chloride is similarly reactive, but also can readily decompose to allyl alcohol. All of the chloroalkenes exhibit varying degrees of reactivity with ozone.

Among the chlorinated aromatics (Table 2), chlorobenzene represented the most volatile (132°C) while benzyl chloride is the least volatile (215°C) of all chemicals tested. Benzyl chloride is also a reactive species in the presence of moisture and thus would be difficult to collect and store accurately.

Benzene and 1,2,3-trimethylbenzene define the vapor pressure range for the aromatic hydrocarbons (Table 2). Some sensitivity to ozone has been shown for these chemicals, the extent of collection problems was to be tested.

The recovery of nitrobenzene and phenol are suspect with polymeric bags and metal containers and thus were included in this study. Also, background from Tenax® GC via ozone exposure producing phenol was to be studied.

The remaining substances (acrylo and sulfur compounds and ethers) are all reactive in the presence of ozone. The stability of Bis-(2-chloroethyl)-ether and α-epichlorohydrin during their collection in the presence of moisture (particularly with HNO_2) was also of interest. The ease of oxidation of methyl mercaptan to dimethyl disulfide was to determine the reactivity of the compound after its collection with inorganic substances.

Thus, the rationale for selecting the compounds in Table 2 is generally obvious. Compounds which were polar and with low vapor pressures were of interest since these substances have a propensity to adsorb to surfaces making quantitative recovery often difficult. Also, they will, when atmospheric conditions are optimum, partition between the aerosol and vapor-phase states. This is particularly important when filtering media are used to remove aerosols/particulates while collecting vapor-phase compounds.

The test compounds listed in Table 2 were used throughout the entire program for the evaluation of FEP Teflon®, Tedlar® (polyvinyl fluoride) and five-layer aluminized plastic bags; glass and metal bulbs; low temperature condensation traps, and charcoal and Tenax ®GC adsorbent traps. The use of a single set of test compounds for evaluating all the collection methods was a major objective since a quantitative comparison between devices was desired.

PERMEATION AND DIFFUSION TUBES

In order to facilitate the evaluation of collection devices, it was necessary to synthesize a continually flowing multi-component vapor/air mixture. The accurate and reproducible synthesis of air/multi-component vapor mixtures had not been reported prior to the initiation of this program. Certified sources of organic vapors in air or permeation tubes for all the chemicals in Table 2 were not available. Thus, the objective of this study was to devise a means of delivering a flow of air/vapor mixture of a known concentration.

To accomplish this, permeation tubes were fabricated and gravimetrically calibrated in this laboratory. Permeation tubes were designed to yield permeation rates for the chemicals in Table 2 to not exceed a range of 50 fold. The details of fabrication and calibration are given in Section 7.

For chemicals with lower vapor pressures than those listed in Table 2, the development of diffusion tubes was an additional objective of this program. This is discussed in Section 10.

PERMEATION/DILUTION SYSTEM

In order to evaluate the collection devices, accurate and reproducible atmospheres of the model compounds were needed. Subsequently one of the objectives of the project was to construct a permeation/dilution system, using permeation tubes and diffusion tubes as sources, to deliver model compounds (1-20 simultaneously) test atmospheres in the range of 10 ppt to 100 ppb. The system was to be designed for laboratory and field experiments and thus be portable. Also, the system was to include a source of "zero" dilution air and was to be designed to minimize loss of the test compounds to the system component walls.

SAMPLING AND ANALYSIS PROCEDURES

As stated, the primary objective of the project was to evaluate the six sample collection devices described previously. This evaluation of the devices cannot be separated from the methods of collecting the samples with the devices and then recovering and measuring the analytes. Another objective then was to develop and/or use the collection, recovery and measurement procedures which are appropriately suited to the collection devices themselves. Also these methods and the collection devices were to be "user friendly" if possible; that is, their use should be practical and within the capabilities of most appropriately trained analysts.

AUTOMATIC SAMPLER

A final major objective of this program was to develop an automatic sampler to be used in an unattended fashion to collect vapor-phase organics on adsorbent-type sampling traps. Specifically, the sampler was to be designed so that it could be preprogrammed for prescribed sampling times and rates, sequentially sampling over long periods of times (a maximum of 24 hr per sample), and the collection of single or duplicate samples. A printout status report for each sample (date, time, volume collected) was to be a feature. The design and fabrication was to include laboratory testing of the sampler and the writing of an operating and maintenance manual.

SECTION 5

DESIGN AND FABRICATION OF PERMEATION/DILUTION SYSTEM

The generation of accurate and reproducible test atmospheres was essential for testing and evaluation of the six collection devices. Prior to initiation of the project, it was proposed that such atmospheres could be produced using permeation and/or diffusion tubes in a permeation/dilution system. The permeation and diffusion tubes were chosen as compound sources as other sources, e.g., compressed gases in cylinders, were not available for the variety of compounds to be used in the study. The permeation and diffusion tubes could be prepared in the RTI laboratories without great difficulty if they were not available from commercial sources. A system was designed to deliver test compound atmospheres in the concentration range at 10 ppt to 100 ppb. The system was intended for both laboratory and field experiments and thus was to be portable. The principle components of the system were to be clean ("zero") air source, the permeation chamber and three dilution stages. The permeation chamber was to be large enough to accomodate about 20 permeation tubes so that mixtures of test compounds could be generated.

SYSTEM FABRICATION

Two systems were constructed. The systems were essentially identical except one contained two dilution stages while the other contained three dilution stages.

A schematic of the system with three dilution stages is shown in Figure 1. In this system, gases emitted from permeation tubes were diluted in a series of steps which each involve removal of a portion of the gaseous sample and addition of diluent (air). Each system was constructed using two Marinite-XL® boxes covered with 0.5 in foil-coated polyurethane foam. The smaller box (Fig. 2) encloses the permeation chamber and a purged storage chamber for the permeation tubes not in use in the chamber. The temperature of

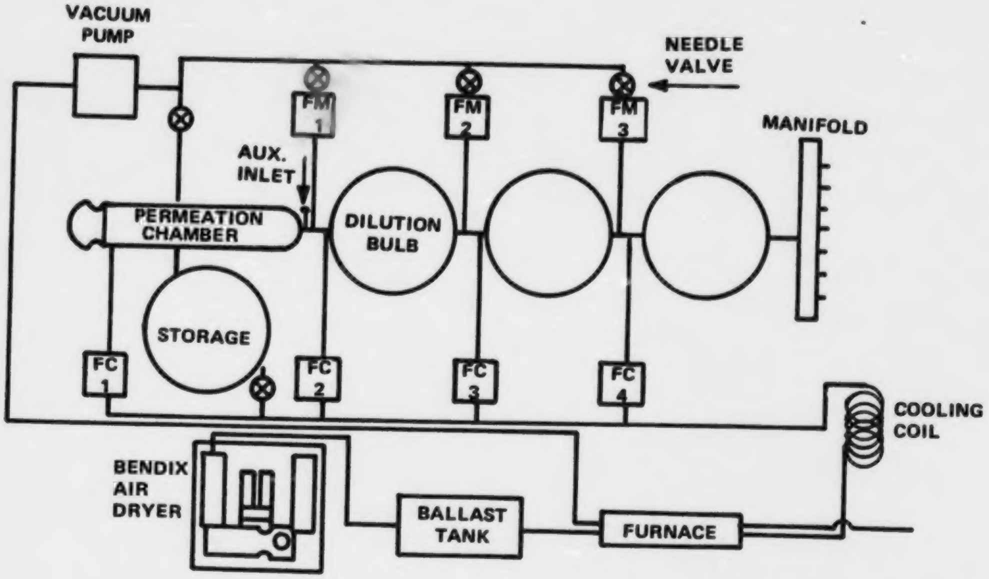
VACUUM PUMP
NEEDLE VALVE
FM 1
FM 2
FM 3
MANIFOLD
AUX. INLET
PERMEATION CHAMBER
DILUTION BULB
STORAGE
FC 1
FC 2
FC 3
FC 4
COOLING COIL
BENDIX AIR DRYER
BALLAST TANK
FURNACE

Figure 1. Overall schematic of permeation system.

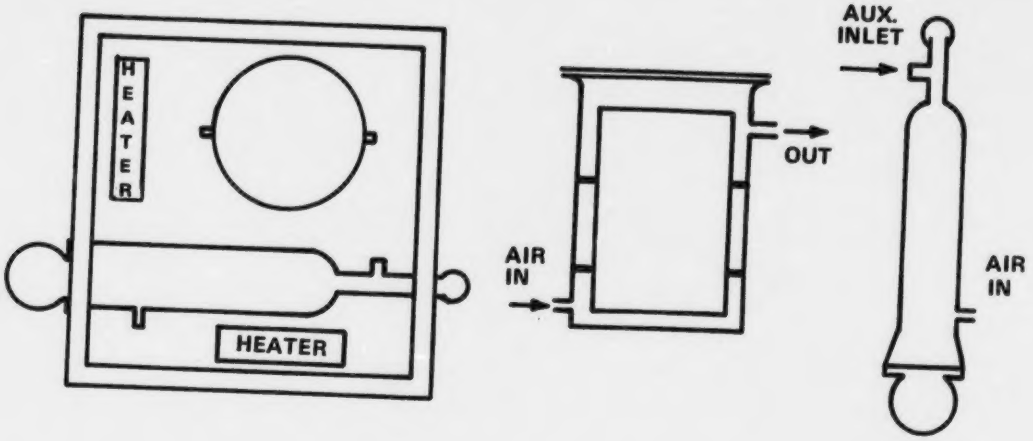
HEATER
HEATER
AIR IN
OUT
AUX. INLET
AIR IN

Figure 2. Permeation chamber, storage vessel, and enclosure.

these permeation tubes was originally controlled through control of the temperature of the air in the box using two ceramic heaters controlled by a Valco precision controller. This was found to be insufficient and the permeation tube chamber was rebuilt so as to be water jacketed. Circulating water at 30.0 ± 0.1°C was provided via a Haake water bath and pump system. The temperature of the dilution air passed into the permeation chamber was controlled by first passing it through several meters of copper tubing setting in the aforementioned water bath. The storage chamber was shock-mounted and was constantly purged with clean air. The purged air was drawn off by the vacuum pump and passed through the catalytic cleaner. The large diameter of the permeation chamber allows several tubes to be inserted at the same time so that complex mixtures may be generated. An auxiliary injection port was added on the outlet of the permeation chamber to allow the injection of radioisotope tracers for the initial studies and also to allow gas mixtures from tanks to be bled to the dilution bulb for further dilution.

The larger component (Fig. 3) houses the three dilution bulbs. These 1 L bulbs were interconnected by 20/12 spherical ground glass joints. A 1000 watt heater and an Omega proportioning heat controller maintained the temperature in the box up to 150°C. A glass manifold distributed the gas mixture to six 0.25" glass sampling ports which passed through the wall of the box. A larger vent port with 25/12 joint passed through the side of the box for disposal of excess mixture.

The permeation system was designed to be portable. As such, it contained its own clean air supply. Air entered the system through the compressor of the Bendix Model 8833 heatless air dryer. The dry air at 60 psi passed into a 12 L ballast tank and then flowed through a platinum/palladium catalyst at 300°C for the oxidation of hydrocarbons. The output from this furnace is allowed to cool by flowing through a 3.5 m length of copper tubing before it reaches the flow controllers. The air is used to dilute the gases given off by the permeation tubes in the permeation chamber. The clean air flows through the chamber after passing through Tylan flow controller (FC) #1, and this mixture then goes into the first dilution stage. An expanded view of the inlet of the dilution bulb is shown in Figure 4.

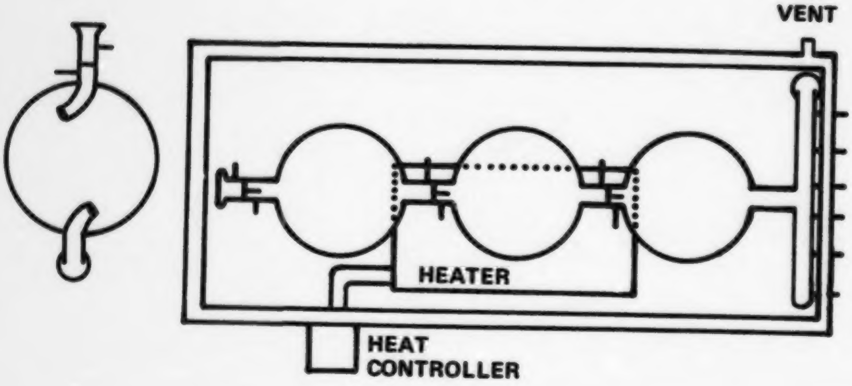
VENT
HEATER
HEAT
CONTROLLER

Figure 3. Dilution bulbs and heated enclosure.

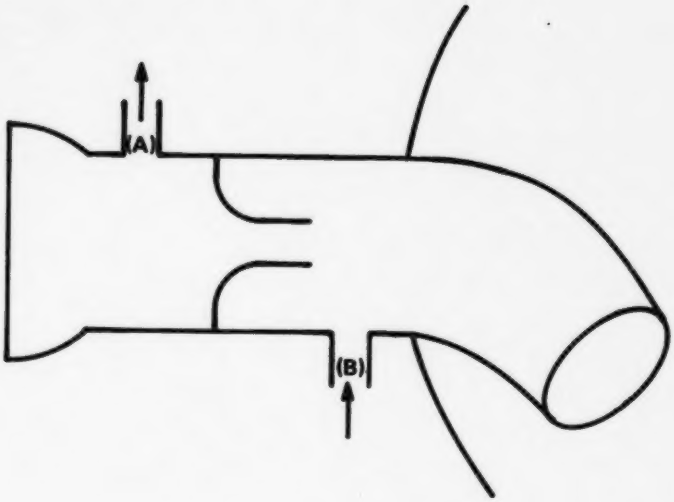

Figure 4. Dilution bulb inlet.

A known portion of the gas mixture could be drawn off at (A, Fig. 4) and passed through the needle valve and flow meter. A known flow of makeup air could be added at (B) for a further dilution. The gas mixture plus dilution air then flows into the mixing bulb. The withdrawal/addition process could be repeated at the next two bulb junctions. Although an infinite dilution of the original gas mixture is theoretically possible, the practical dilution limit of this system was originally considered to be 10^6. The entire process can be illustrated through an example. If a permeation tube gives off a compound at 1 μg/min, and the flow across the tube from FC #1 is 1 L/min, the concentration at the outlet of the permeation chamber if 1 μg/L. If 990 mL/min of this flow is taken at point A through FM #1 and 990 mL/min air is added at B, the mixture in the first dilution bulb should be 0.01 μg/ℓ concentration. This dilution of 1:100 at each stage was originally considered the maximum that should be attempted with this system. If this maximum dilution were achieved at each of the three stages, the final output concentration will be one one-millioneth of the concentration at the outlet of the permeation chamber. After some initial trials with the system, this dilution factor was found to be overly optimistic. The principal difficulty arises from reproducibly withdrawing a large quantity of test atmosphere at each dilution stage. Needle valves rather than electronic flow controllers were used to control test atmosphere removal as flow controllers do not work well with less than 10 psi difference across the input to the output sides of the controller. Greater than 10 psi pressure drop is very difficult to maintain when withdrawing large volumes of gas, unless an especially high volume vacuum pump is used. Needle valves are reproducible to about ±1 percent. Following the example given above, 990 ± 10 would be withdrawn, leaving great uncertainty in the amount remaining. Subsequently, it was concluded that factors of 10-20 (maximum) per dilution stage were much more practical. Again following the example, 900 ± 10 would be withdrawn leaving 100 ± 10 mL to be diluted to 1000 mL for a dilution factor of 10. Also, the Tylan flow controllers and meters were compared to NBS traceable bubble flow meters and found to be 10-20% off in all cases. They were then calibrated using the bubble flow meters as standards rather than attempting to make a correction for the type of gas being used or some other mathematical correction.

An initial problem was experienced with the air compressor/dryer enclosure which caused overheating of the pump motor. The compressor/dryer was subsequently operated without an enclosure.

VALIDATION OF PERMEATION/DILUTION SYSTEM

Radiolabeled compounds were employed for validation of the portable permeation system. Initial testing was conducted to determined the extent of condensation in the permeation system of a non-polar high boiling compound at relatively high concentrations (>100 ppb). For this purpose, n-[1,2 (n)-^{3}H] hexadecane with a specific activity of 4.86 x 10^6 dpm/g was procured from Amersham Corporation. n-Hexadecane (b.p. 287°C) has a density of 0.773 g/mL, so that 4.7 μL injected was equivalent to 3.6 mg which produced 16,600 dpm. A TriCarb® scintillation counter (Packard Inst., Chicago, IL) was used.

The permeation system was assembled and calibrated; the permeation chamber temperature was brought to 30°C, and the secondary dilution system brought to 65°C. The hydrocarbon free air flowed at 250 mL/min. Four midget impingers each containing 10 mL of Triton X scintillation counting solution were connected in series downstream of the dilution for collection of the labelled compounds. Then 4.7 μL of radiolabeled n-hexadecane was introduced into the system using a 10 μL syringe (Run A). Collection was effected for 60 min, at which time a new set of impingers was put in line. The temperatures of the permeation chamber and the dilution system were increased to 60°C and 93°C, respectively, and another 4.7 μL of the radiolabeled hexadecane was injected (Run B). This collection continued for 60 min, at which time new impingers were placed in line. The flow was increased to 1000 mL/min, the temperature of the permeation chamber and dilution system was reduced to initial conditions, and the effluent collected for another 60 min period (Run C). The permeation chamber was then removed from the system and rinsed with a 2 mL aliquot of toluene. This was added to Triton-X scintillation counting solution and counted along with the samples from the impinger. Results are listed in Table 3. The permeation system

Table 3. RECOVERY OF RADIOLABELED n-HEXADECANE FROM PERMEATION SYSTEM

Run No.	Quantity Injected (dpm)	Collection Set	Dpm Observed (collected)
A	16,000	1	1,192
B	16,600	2	7,102
C	0	3	2,509
		Toluene Rinses	14,832
		Total	25,635

was then disassembled and thoroughly washed and dried to remove residual radiolabeled compounds.

Due to the low recovery of the tritiated hexadecane, radiolabeled ^{14}C-bromobenzene (b.p. 156°C) was selected for further system condensation testing. The radioisotope was diluted to a specific activity of 1,335 dpm/μL so that a 5 μL injection equivalent to 7.5 mg of bromobenzene-contained 6,675 cpm. The permeation chamber was brought to 60°C the dilution system was at 65°C, and the hydrocarbon free air flowed at 250 mL/min.

The radioisotope was injected (Run A, Table 4) into the system and the effluent collected at 250 mL/min in the impingers containing 10 mL of Triton X scintillation counting solution. After 60 min, these were removed and replaced by a second set of impingers which collected for another 60 min. These aliquots were then counted, and a total of 105% recovery was observed.

Duplicate injections (Run B and C, Table 4) of bromobenzene were then made with the temperature of the permeation chamber at 30°C and all other parameters remaining unchanged. As before, the effluent was collected at 250 mL/min and counted. Yields of 92% and 87% were observed.

The low concentration condensation experiment was executed using radiolabeled ^{14}C-bromobenzene in methanol, 90 μg/μL with a specific activity of 5,838 dpm/μL. Duplicate injections (Run D and E, Table 4) of 1 μL-equivalant to 6 ppt were delivered into the permeation chamber which was at 30°C. The secondary dilution system was at 65°C, and again the flow rate was 250 mL/min. These two injections netted 88 and 83% recoveries.

Thus, from these experiments, it appears that the permeation/diluter system is acceptable for yielding high recoveries of semi-polar to non-polar compounds that have boiling points of up to ~160°C.

The adsorption of volatile polar compounds onto the glass surface of the permeation/dilution system was the subject of further investigation. This was done with ^{14}C-diethylamine hydrochloride in water, which had a specific activity of 60 dpm/μL and a concentration of 4 ng/μL.

The permeation system was disassembled, washed with Alkonox® followed by Isoclean®, rinsed with deionized water, baked overnight at 400°C, and then reassembled. Thirty microliters of the diethylamine hydrochloride in water were injected onto a glass wool plug impregnated with potassium hydroxide

Table 4. RECOVERY OF ^{14}C-BROMOBENZENE FROM PERMEATION SYSTEM

Run No.	Quantity Injected (dpm)	Impinger Set	Dpm Observed (collected)	Percent Recovery
A	6,672	1	6,433	106
		2	606	
B	6,672	1	6,142	92
		2	31	
C	6,672	1	5,794	88
		2	64	
D	5,838	1	5,157	89
		2	24	
E	5,838	1	4,864	84
		2	36	

in the gas stream of the permeation chamber. The resulting reaction yielded the free base diethylamine (b.p. 56.3°C). The permeation chamber was heated to 30°C, the dilution system was at 65°C, and the hydrocarbon free air flow set at 250 mL/min. The effluent gas stream was bubbled through 4 impingers in series, each containing 10 mL of the Triton-X scintillation counting solution. Subsequent analysis of the cocktail indicated no significant amount of the ^{14}C-diethylamine to be collected from the permeation/diluter system. The glass wool plug was removed from the system and placed in cocktail and counted. Radiation level for the glass wool was 33 counts/min above background indicating the radiolabeled compound was released into the gas stream and had apparently adsorbed onto the interior surfaces of the glass system. Collection of radiolabelled diethylamine in the 4 midget impinger arrangement was verified by injecting the compound directly in front of the collection assembly fitted with a heated injection port and gas flow at 250 mL/min.

Deactivation of the adsorption sites on the glass surfaces of the permeation/diluter system was attempted utilizing N-methyl-N-trimethylsilyl-trifluoroacetamide (MSFTA). A 10% mixture of the low boiling silanizing agent in methylene chloride was prepared and three 10 µL injections at 20 min intervals were made into the permeation system through the 70/60 injection stopper unit. The chamber temperature was 65°C, the dilution system was set at 150°C and the hydrocarbon free air was set at 250 mL/min and was maintained in this stage for 18 hrs following the final injection.

Following silanization, the radiolabel diethylamine experiment was conducted as before. Again, no significant amount of the radioisotope passed through the permeation/dilutier system.

Following another silanization step, the radiolabel diethylamine experiment was conducted as before. Again, no significant amount of the radioisotope passed through the permeation/diluter system.

The system was again disassembled and cleaned with Isoclean®, rinsed with deionized water, and baked at 400°C overnight. The interior of the glassware was washed with a solution of 0.1% Carbowax 20M in methylene chloride and baked at 280° for 2 hrs while being purged with nitrogen gas. After cooling to room temperature, it was again treated with 0.05% Carbowax

20M in methylene chloride and again baked for 2 hrs at 280°C with nitrogen gas purged. The diethylamine experiment was again conducted with no apparent recovery of the isotope.

Two subsequent treatments with the Carbowax 20M followed by the diethylamine radioisotope experiment indicated adsorption continued to be a problem.

Solutions of 0.1% and 0.05% Carbowax 20M and toluene were made and used in an attempt to reduce the adsorption onto glassware. The subsequent diethylamine experiment indicated no improvement in the adsorption problem.

Since the first group of model compounds were semi- and non-polar, the problems associated with the glassware in the permeation/dilution system were expected to be minimal and primarily influenced by condensation and not adsorption. Thus the project proceeded with the system described. It was anticipated that the system would be possibly modified when the low-volatility, polar compounds were to be studied. These compounds were never studied however.

TEST ATMOSPHERE GENERATION

When the permeation/dilution system was first used to generate standards, poor reproducibility was noted in the concentrations generated. After study of the permeation/dilution system, several ideas for improvement of the precision of the system were arrived at. These ideas were as follows:

A. Temperature Control

   (1) The water-jacketed permation tube chamber and the dilution bulbs should be at the same temperature.

   (2) The temperature of the entire system should be controlled to ±0.1°C.

   (3) Both the perm tube chamber and the tube bringing "zero" air from the constant-temperature water bath should be well insulated. Also, this tube should be Teflon and not copper.

B. Input and Output Flows of the Dilution Stages

   (1) Flows should be measured with a bubble flow meter before and after use of the dilution system. Flow controllers may be used to monitor drifts but readings from these devices cannot be accepted as absolute values.

(2) Flow controllers should only be used to control flows in the range of 10%-90% of the designated controller range.

C. Miscellaneous

(1) Addition of ground glass joints to the tubes on the bulbs through which dilution gas is added and gas is removed was considered. The initial system used Swagelok® fittings to make the connections. This change, which would have made bulb removal for cleaning easier, was not implemented.

(2) The dilution system should not be used to generate low-concentration samples following generation of high-concentration samples without first cleaning the bulbs.

Not all these ideas could be implemented. The dilution bulbs need to be maintained at about 150°C to minimize loss of sample to the glass. Also, though the permeation tube chamber is maintained at ±0.1°C, this could not be done with the dilution bulbs, where temperature control was about ±0.5°C.

SECTION 6

EVALUATION OF SAMPLE COLLECTION DEVICES

INTRODUCTION TO EXPERIMENTAL DESIGN

The experimental design called for collection of various test mixtures of compounds using six primary collection devices and then recovery and measurement of these compounds. Various parameters were to be varied while others were to be held constant. The relationships of these test parameters were shown in Table 1. In experimental design A (Table 1), the sampling volume and relative humidity (30%) were to be held constant. The variable parameters were to be the concentration of each individual compound, and the storage time. The compound concentrations were to be zero, not less than 10 ppt (low) and not more than 100 ppb (high). In the second experimental design (B), the sampling volume, ozone, SO_2 and NO_x concentrations and the relative humidity were to be varied while the sampling time and rate and test compound concentration were to be constant. The interferent concentrations were to be as follows: relative humidity -30% and 90%; SO_2 -∿10 and ∿200 ppb; NO_x - ∿100 and ∿500 ppb and O_3 - ∿75 and ∿500 ppb. These concentrations reflect low and high ambient levels of SO_2, NO_2 and O_3.

As stated previously the six collection devices were to be polymeric bags, steel cannisters, glass bulbs, cryogenic traps and Tenax and charcoal adsorbent traps. The containers and traps were to be tested principally for their ability to retain the input level of concentration. Three levels of concentration (zero, low, high) were to be utilized and measurements of concentration were to be made at three points in time (t_o, t_1, t_2). The layout of the design for the planned study was shown in Table 5. It was intended that analysis of variance be applied to the data resulting from this set of measurements to determine the mean differences among the types of sampling devices. Table 6 presents the design layout for determining effects of humidity, SO_2, NO_x and O_3 on high concentration samples.

Table 5. EXPERIMENTAL DESIGN FOR OBTAINING MEASUREMENTS ON THREE LEVELS OF CONCENTRATIONS (ZERO, LOW, HIGH) AT THREE POINTS IN TIME (t_0, t_1, t_2) USING THREE CONTAINER TYPES[a]

		Zero			High			Low		
Collection Device	Sample No.	t_0	t_1	t_2	t_0	t_1	t_2	t_0	t_1	t_2
Tedlar Bag	1	X	X	X						
	2	X	X	X						
	3	X	X	X						
	4				X	X	X			
	5				X	X	X			
	6				X	X	X			
	7							X	X	X
	8							X	X	X
	9							X	X	X
Stainless Steel Can	1	X	X	X						
	2	X	X	X						
	3	X	X	X						
	4				X	X	X			
	5				X	X	X			
	6				X	X	X			
	7							X	X	X
	8							X	X	X
	9							X	X	X
Glass Bulb	1	X	X	X						
	2	X	X	X						
	3	X	X	X						
	4				X	X	X			
	5				X	X	X			
	6				X	X	X			
	7							X	X	X
	8							X	X	X
	9							X	X	X

(continued)

Table 5 (cont'd.)

Collection Device	Sample No.	Zero			Low			High		
		t_0	t_1	t_2	t_0	t_1	t_2	t_0	t_1	t_2
Low Temperature Condensation Trap	1	X	X	X						
	2	X	X	X						
	3	X	X	X						
	4				X	X	X			
	5				X	X	X			
	6				X	X	X			
	7							X	X	X
	8							X	X	X
	9							X	X	X
Charcoal Adsorbent Trap	1	X	X	X						
	2	X	X	X						
	3	X	X	X						
	4				X	X	X			
	5				X	X	X			
	6				X	X	X			
	7							X	X	X
	8							X	X	X
	9							X	X	X
Tenax Adsorbent Trap	1	X	X	X						
	2	X	X	X						
	3	X	X	X						
	4				X	X	X			
	5				X	X	X			
	6				X	X	X			
	7							X	X	X
	8							X	X	X
	9							X	X	X

[a] Concentration levels and storage time were tested. Three replicates are included for each concentration.

Table 6. EXPERIMENTAL DESIGN FOR DETERMINING EFFECTS OF HUMIDITY, SO_2, NO_x, AND O_3 ON HIGH CONCENTRATION SAMPLES[a]

Collection Device	Sample No.[b]	Experiment 1B	Experiment 2B
Tedlar Bag	10	X	
	11	X	
	12		X
	13		X
Stainless Steel Can	10	X	
	11	X	
	12		X
	13		X
Glass Bulb	10	X	
	11	X	
	12		X
	13		X
Low Temperature Condensation Trap	10	X	
	11	X	
	12		X
	13		X
Charcoal Adsorbent Trap	10	X	
	11	X	
	12		X
	13		X
Tenax® GC Cartridge	10	X	
	11	X	
	12		X
	13		X

[a] Sample volume, ozone, SO_2, and NO_x concentrations, relative humidity are the test parameters.

Experimental Design 1B	O_3	~500 ppb
	SO_2	~200 ppb
	NO_x	~500 ppb
	RH	~90%
Experimental Design 2B	O_3	~75 ppb
	SO_2	~10 ppb
	NO_2	~100 ppb
	RH	~30%

[b] Samples will be collected in triplicate.

The experimental design for testing the cryogenic trap and the charcoal and Tenax sorbents is essentially identical to that shown for the containers. The principal difference between the containers and these devices is that replicate samples can be drawn from each container whereas only one sample can be recovered from the trap and sorbents. Thus, 6 samples/experiment were collected for each concentrating sampling device.

EXPERIMENTAL PROCEDURE

Sample Collection

Bags--

Three types of polymeric bags were selected for evaluation. These were FEP Teflon, Tedlar (polyvinyl fluoride) and five-layered aluminized bags. Polymeric bags present the greatest challenge as contamination can arise from the walls of the bag, from the polymeric material itself and from diffusion into the bag from the outside environment.

Cleaning--The cleaning procedure originally proposed and utilized involved several cycles of evacuating and filling the bags with clean air. This procedure worked generally well for Teflon® and Tedlar® bags. The five-layer bags could not be cleaned to any reasonable degree and thus were eliminated from the study. The cleaning procedure described above sometimes failed even with Teflon® and Tedlar® and thus some different cleaning procedures were tested. The four bag-cleaning methods investigated were: (1) evacuation of contaminated contents; (2) clean air flushing; (3) clean air flushing plus direct sunlight irradiation; and (4) clean air flushing plus ozonation and direct sunlight irradiation.

Four Tedlar® and four Teflon® 10 liter bags (2 and 5 mil thickness) were used for evaluation of the clean-up methods. These bags were prepared with sheet polymer provided by the EPA; the bag seals were made using a Vertrod (Brooklyn, NY) thermal impulse heat sealer. Each prepared bag was filled with clean air containing approximately one part per million of an aromatic-aliphatic hydrocarbon mixture. After several hours, each bag was evacuated and refilled with clean air. The following day, the contents of one Tedlar® and one Teflon® bag which had not been flushed previously were chromatographed. A second set of one Tedlar® and one Teflon® bag were flushed two times with clean air and then their contents were chromatographed.

Another set was flushed two times with clean air, filled with clean air, and irradiated in direct sunlight. A fourth set of Tedlar® and Teflon® bags was flushed twice with clean air, filled with approximately 25 parts per million ozone, and irradiated in direct sunlight. After several hours, the irradiated bags were evacuated and refilled with clean air. The following day, these remaining four bags were flushed two times with clean air and their contents chromatographed.

Data acquired showed that the clean air flush was sufficient in removing the majority of the volatile compounds from the Tedlar® bags. The total chromatographic peak area measured with samples taken from the cleaned bags was found to be about two to four times that measured with samples of clean laboratory air. This peak area level corresponds to about 1-2 ppb C. A reduction to near non-detectable levels is observed with clean air plus irradiation and little additional clean-up is gained with ozonation plus irradiation.

The low molecular weight compounds were easily removed from Teflon® with clean air flushing but the heavier aromatic hydrocarbons were not. It appears that a minimum of clean air flush plus irradiation is necessary to clean Teflon® bags satisfactorily. Ozonation plus irradiation is required to remove all compounds to near non-detectable level.

Sampling Procedure--For polymeric bags, a typical field application involves pumping sample into the bag through a metal bellows pump or placing the bag in an airtight vessel with the inlet of the bag exposed to a sample port, then evacuating the enclosure vessel to fill the bag. Passing the sample through a stainless steel bellows pump could introduce a new variable into the evaluation if any of the species in the mix reacted with stainless steel. In order to avoid this complication, the mixture should enter the bag directly from the sample port with no metal contact. In this program the bags were attached to the glass manifold of the permeation/dilution system with TFE Teflon® fittings and allowed to fill by the pressure of the system.

Glass Bulbs--

The glass bulbs used in this project were prepared from 2 liter, round-bottom Pyrex glass flasks to which had been attached Teflon, high vacuum stopcocks. Six mm glass tubing was attached to the second port of each stopcock so that connection could be made with a Swagelok® fitting to metal and/or polymeric tubing.

Cleaning--The procedure originally proposed and utilized for cleaning glass bulbs was complex. The vacuum stopcocks were removed and the glass bulbs were rinsed with a mixture of potassium dichromate and sulfuric acid, rinsed several times with distilled water and then placed in an oven at 400°C for 24 hours. The bulbs were then evacuated, flushed with clean air and heated three times each. A major problem encountered with the glass bulbs was their fragility. Bulb input/out tubes were broken numerous times while removing the stopcocks. It was thus decided that the cleaning procedure for bulbs should consist of several cycles of filling the bulbs with clean air and then evacuating them while the bulbs were heated to a temperature of about 150°C. Viton® o-rings must be used for the stopcocks. Other materials will decompose and give rise to contaminants at this temperature.

Sampling Procedure--Typically glass bulbs are sent to the field evacuated and then simply opening a stopcock to obtain a sample. This method however, would not provide enough sample for the repetitive analyses to be performed. Thus the glass bulbs were filled by means of a metal bellows pump. The upstream side of the pump was connected to the output manifold of the permeation/dilution system. The downstream side of the pump was then connected to the bulb by means of metal tubing and a Teflon, Swagelok fitting. A small pressure gauge on a T connected to this tube indicated bulb pressure. The bulbs were filled to about 15 psi (above ambient pressure). They were not filled above this pressure as a matter of safety.

Cannisters--

Two types of steel cannisters were evaluated. One type was prepared in the RTI laboratory. The bodies of these containers as well as the tops were made from 304 stainless steel. The container bodies were constructed from a 2-L stainless steel beaker manufactured by Vollrath (Sheboygan, Wisconsin). The beakers were electropolished by filling them with a 1:1 (w/w) mixture of concentrated sulfuric and phosphoric acids and applying a 6-volt charge at 8 amps, using the beaker as a cathode and a tin bar immersed in the acid mixture as the anode. The tops of the containers were 1/8 inch (3.175 mm) thick stainless steel. The lips on the stainless steel beakers were cut with a wet cutting wheel after the containers had been electropolished. After the container was cut, it was cleaned with strong oxidizing reagents (Nochromix, Godax Labs) to remove any grease deposits on the inside of the container.

A 1/4 inch (6.35 mm) x 2 inch (50.8 mm) stainless steel tube was heliarced to the top of each container. The tops were then electropolished, and the tops and bodies of the containers were joined by heliarcing under an inert atmosphere to prevent any oxidation of the interior surfaces during this process. The containers were then mounted with H series Nupro valves constructed of stainless steel with metal bellow seals. Each container was then engraved with a letter and number. The container was then ready for testing. It was first pressurized to 60 psi with zero air and leak checked. The container was immersed in clear water and visually inspected for leaks. If there were no leaks, the container was ready to be cleaned.

The second type of steel container evaluated was the "Summa®" polished stainless steel container manufactured and sold by D&S Instruments Ltd., Pullman, WA. Summa® is a proprietary electropolishing method of Molectrics Corp. These 6 L containers are spherical with a cylindrical base welded to each to serve as a stand. Each container is mounted with a single input/output tube to which is attached two H series Nupro valves in a T configuration.

Cleaning--The cleaning of the steel cannisters consisted of several cycles of filling with clean air and then evacuating while under conditions of high temperature. Four containers at a time were connected to a manifold in a Marinite® box fitted with a large heating element and a temperature controller from RFL Industries, Inc. (Boonton, NJ). The manifold was valved so that either vacuum could be applied or clean air could be introduced. The temperature in the box was raised to 150°C. The containers were then evacuated to less than 0.5 mm Hg pressure and maintained at that condition for 1-2 hours. The containers were then filled with clean air to a pressure of about 60 psi and maintained at that condition for 1-2 hours. The containers were then evacuated once again and the whole cycle repeated. Generally 4-5 cycles were sufficient for cleaning. At the conclusion of the last cycle, the containers were evacuated in preparation for sample collection.

Sampling Procedure--The steel cannisters were loaded with test gases from the permeation/dilution system using a metal bellows pump (Metal Bellows Corp., Model MB-151). All connections from manifold to pump and from pump to container were made with stainless steel or Teflon® connectors and tubing. The containers were filled at a rate determined by a critical orifice placed between the pump and the container, which was about 300 mL/min. The containers were filled to a pressure of about 15 psig.

Tenax GC Cartridges--

Preparation--Virgin Tenax® GC (Applied Science, State Park, PA) was extracted in a Soxhlet apparatus for a minimum of 18 hr with methanol prior to its use. The Tenax® GC sorbent was dried in a vacuum oven at 100°C for 3-5 hr and then sieved to provide a fraction corresponding to 35/60 mesh. This fraction was used for preparing sampling cartridges.

The sampling tubes were prepared by packing a 10 cm long x 1.5 cm i.d. glass tube containing 6.0 cm of 35/60 mesh Tenax® GC with glass wool in the ends to provide support. Cartridge samplers were then conditioned at 270°C with helium flow at 30 mL/min for 30 min. The conditioned cartridges were transferred to Kimax® (2.5 cm x 150 cm) culture tubes, immediately sealed using Teflon-lined caps and cooled. The culture tubes were placed in sealable cans to provide a second seal during storage. This procedure was performed in order to avoid recontamination of the sorbent bed.

Sampling Procedure--The sampling cartridges were assembled as shown in Figure 5. The Teflon Swagelok union was attached to the small diameter (0.25 in o.d.) end of the cartridge in a 416 Beckman union fitted with a Luerlok® was fitted to the other end. The hypodermic needle was attached to the Luerlok® and the 0.25 in Teflon® Swagelok® was tightened to the manifold of the permeation/dilution system. Sampling at 1 L/min was then initiated. After sampling of 30 L of air from the permeation/dilution system (blank) or the air-vapor mixture, the Tenax cartridges were returned to the Kimax® culture tubes. All sampling cartridges were handled with Kimwipes® or clean tweezers to avoid their contamination.

Charcoal Cartridges--

Preparation--NIOSH charcoal tubes (200 mg) were purchased from Supelco (Belfonte, PA) and used in these experiments as received.

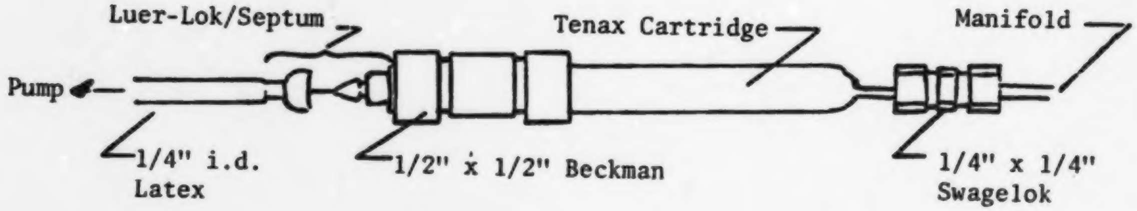
Luer-Lok/Septum
Tenax Cartridge
Manifold
Pump
1/4" i.d. Latex
1/2" x 1/2" Beckman
1/4" x 1/4" Swagelok

Figure 5. Tenax cartridge sampling arrangement employed with permeation/dilution system.

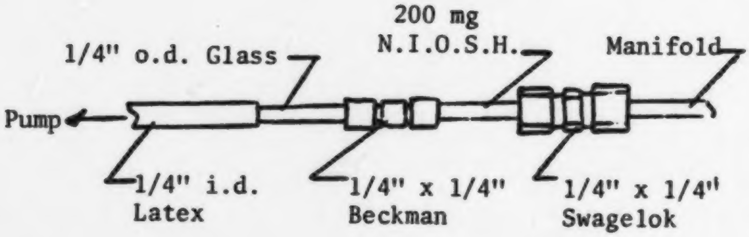
200 mg N.I.O.S.H.
1/4" o.d. Glass
Manifold
Pump
1/4" i.d. Latex
1/4" x 1/4" Beckman
1/4" x 1/4" Swagelok

Figure 6. Charcoal cartridge sampling arrangement employed with permeation/dilution system.

Sampling Procedure--Figure 6 depicts the devices associated with connecting the charcoal sampling tube to the permeation/diluter system. A total of 30 L of the synthetic air-vapor was sampled at 1 L/min.

Cryogenic Traps--

Preparation--Cryogenic traps were made of 0.25 in o.d. 0.21 in i.d. nickel tubing in 24 in lengths. Traps were coiled in a transaxial configuration (Fig. 7). Cryogenic traps were cleaned with methanol and pentane to remove cutting oil and then thermally conditioned at 160°C under helium flow (~30 mL/min) for 2 hr. Initially the cryogenic traps were used empty. Subsequently, when recoveries were observed to be low, they were filled with clean 2 mm glass beads and used with liquid oxygen as the cryogen. Upon cooling (under flow), the nickel traps were immediately sealed with Swagelok® fittings. The helium used during conditioning of the traps as well as for purging the contents onto Tenax cartridges was passed through a liquid nitrogen cryogenic trap to remove impurities, a step found to be essential to achieve a low background.

Sampling Procedure--The configuration for collecting vapor-phase organics using nickel cryogenic traps is shown in Figure 8. A transaxially coiled trap was employed and the cryogenic trap was immersed midway into finely crushed dry ice or, in later experiments, liquid oxygen. The opened end of the quick-connect, the 0.25 in x 0.5 o.d. glass adaptor, and the 416 Beckman were assembled as shown in Figure 7. One end of the trap was attached to the pump while the other end was attached to the manifold of the permeation/dilution system with a Teflon® union. The nickel traps were then set in the cryogenic medium which cooled only half of these transaxial traps. This configuration was used while collecting 30 L of the test air-vapor mixture at 1 L/min. After sampling, the quick-connect fitting was removed and the end was capped immediately. The nickel trap was removed from the cryogenic bath and placed in a container of dry ice for storage. No solvents were employed throughout the collection and analysis of the cryogenic traps.

Measurement Procedure

Bags, Bulbs, and Cannisters--

Recovery--The recovery and measurement procedure was identical for samples in bags, glass bulbs, and steel cannisters. The container is first

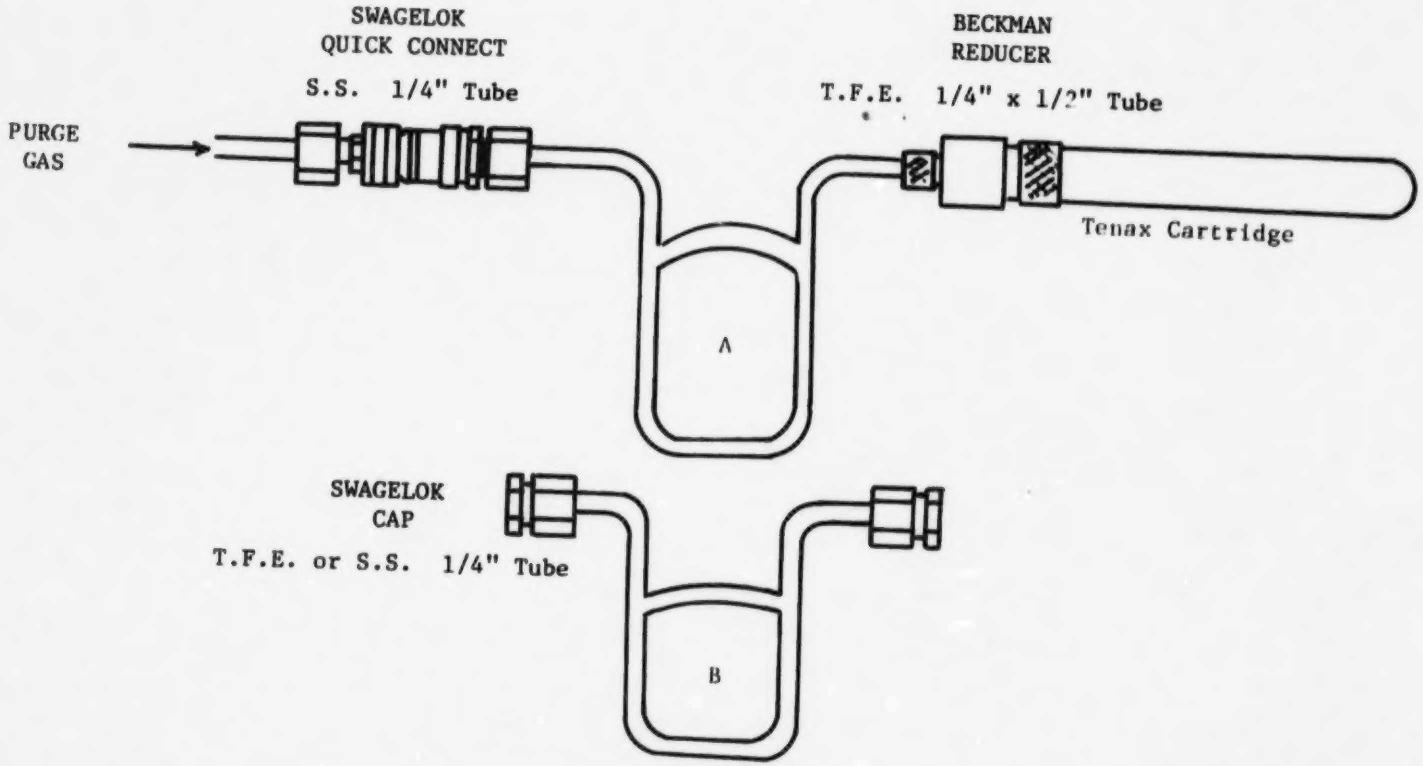
SWAGELOK
QUICK CONNECT
S.S. 1/4" Tube
BECKMAN
REDUCER
T.F.E. 1/4" x 1/2" Tube
PURGE
GAS
Tenax Cartridge
A
SWAGELOK
CAP
T.F.E. or S.S. 1/4" Tube
B

Figure 7. Purging (A) and storage arrangements (B) for recovering vapors from Ni traps.

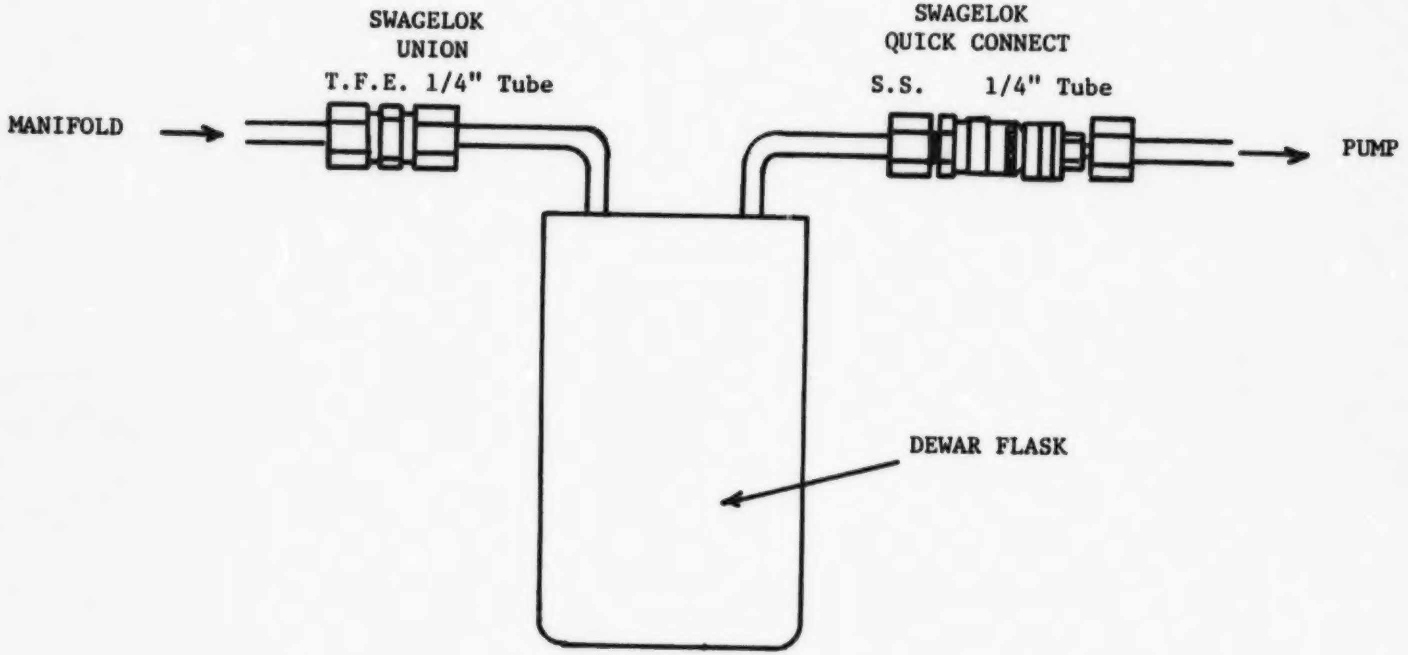
SWAGELOK
UNION
T.F.E. 1/4" Tube
SWAGELOK
QUICK CONNECT
S.S. 1/4" Tube
MANIFOLD
PUMP
DEWAR FLASK

Figure 8. Nickel cryogenic trap sampling arrangements employed with permeation/dilution system.

placed in a box and loosely connected via a Swagelok fitting to a heated sample transfer line as shown in Figure 9. The box could be heated and was done so for the glass and steel containers but not the bags; the temperature used for the glass and steel containers ranged from 50° to 90°C. Valve A is opened and the inlet line is purged with clean air. At this point, the entire system can also be purged. After the lines have been purged, valve A is closed and the connection to the container immediately tightened. The multiposition valve is turned to the sample loop, and the corresponding outlet valve (C) is opened. The sample loop used was a 15 cm length of 1 mm i.d. stainless steel tubing in the shape of a U filled with glass beads. Valves D and E are opened to evacuate the entire system and the sample loop is immersed in liquid oxygen. Then valve D is closed, the container valve is opened and the heated metering valve (B) is opened to allow sample to enter the system.

The amount of sample passed through the sample loop is determined by the pressure change on the Heise gauge. For cryogenically trapped samples, the following equation is used.

$$V = \frac{V_d \Delta P}{P_a}$$

V = gas volume passed through trap (mL)
V_d = total dead volume in the system (this was 536 mL in our system)
ΔP = pressure change registered on gauge (mm Hg)
P_a = ambient barometric pressure (mm Hg)

A typical sample volume was 200 mL. After the sample was trapped in the cryogenic loop, the liquid oxygen Dewar was removed, and a heated silicone oil bath (150°C) was substituted for this Dewar. This sudden heating caused flash volatilization of the trapped organic compounds. Rotation of the valve resulted in carrier gas sweeping the sample into the gas chromatographic column.

The measurements were performed with a Perkin-Elmer Model 3920 gas chromatograph modified to accept a 30 meter SE-30 SCOT column. The GC system included a column effluent splitter to allow simultaneous FID and EC detection of the mixture components. The FID and EC responses were recorded

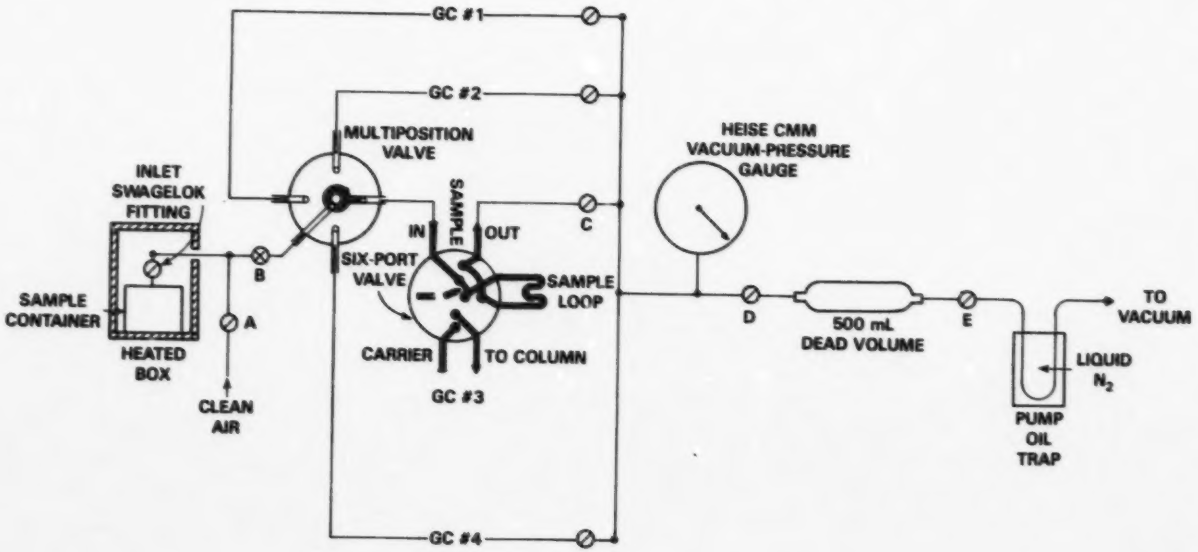
GC #1
GC #2
MULTIPOSITION VALVE
INLET SWAGELOK FITTING
SAMPLE CONTAINER
HEATED BOX
B
A
CLEAN AIR
SAMPLE
IN
OUT
SIX-PORT VALVE
SAMPLE LOOP
CARRIER
TO COLUMN
GC #3
GC #4
C
HEISE CMM VACUUM-PRESSURE GAUGE
D
500 mL DEAD VOLUME
E
TO VACUUM
LIQUID N_2
PUMP OIL TRAP

Figure 9. Vacuum injection manifold.

Analysis:
1. Sample placed in heated enclosure.
2. 100 mL portion passed through cryogenic traps.
3. Flash desorption onto column.

on a dual pen strip chart recorder. The outputs of the two detectors were also connected to analog-to-digital converters which are part of a Hewlett-Packard 3352B laboratory data system. Peak retention times and areas were determined by the computer and printed out in tabular form. The gas chromatographic parameters used are listed in Table 7.

Calibration--Calibrations were performed for each group of compounds. The FID response was standardized at three different compound concentrations by drawing a sample directly from the glass manifold through a heated 1/8" O.D. stainless steel sample line into the GC sampling system. Each concentration was calculated based upon the permeation rate of the compound, the chamber air flow, and the dilution air flow. Typical concentrations used in establishing standard curves and the correlation coefficient for each compound response curve are given in Section 7 in Tables 47 and 48.

As the results indicate, furan and acrylonitrile were not resolved on the GC system used in this study. A percent recovery for furan plus acrylonitrile is given for the "Summa" polished cans as well as the other containers studied.

Tenax® GC Cartridges and Cryogenic Traps--

Recovery--The instrumental conditions for the thermal desorption/gas chromatographic analysis of volatile organics on Tenax® GC sampling cartridges are given in Table 8. The inlet-manifold system is depicted in Figure 10. The thermal desorption chamber and the six-port Valco® valve were maintained at 270°C. The helium purge gas through the desorption chamber was adjusted to 15 mL/min. The Ni capillary trap on the inlet manifold was cooled with liquid nitrogen. In a typical thermal desorption cycle, a sampling cartridge was placed in the preheated desorption chamber and helium gas was passed through the cartridge to purge the vapors into the liquid nitrogen capillary trap. After the desorption was completed, the six-port valve was rotated and the temperature on the capillary loop was rapidly raised. The carrier gas then introduced the vapors onto the high resolution GC column. The glass capillary column was temperature programmed under the conditions listed in Table 8. After all of the components had eluted from the column, the column was cooled to ambient temperature and the next sample was processed.

Table 7. CHROMATOGRAPHIC PARAMETERS FOR ANALYSIS OF CONTAINERS

Parameters	Setting Conditions
Column	30 m SE-30 SCOT; 0.5 mm i.d.
Carrier Gas	He - 5 mL/min
Make-up Gas	He - 23 mL/min for FID
	Ar/CH_4 - 15 mL/min for ECD
Column Temperature	0°C/4 min, 4°C/min, 150°-0 min
FID - Air flow - H_2 flow	40 psi 17 psi
GC	Perkin Elmer Model 3920
Detector Temperature	200°C

Table 8. OPERATING PARAMETERS FOR THERMAL DESORPTION AND GC/FID OF TENAX CARTRIDGES

Parameter	Setting
Inlet Manifold	
Desorption chamber and valve	270°C
Capillary trap - min	-195°C
- max	240°C
Desorption time	8 min
He purge flow	15 mL/min
GLC	
65 m glass SCOT SE-30; 0.50 mm i.d.	40°C for 6 min, 40-210°C, 4°C/min
Carrier (He) flow	~2.5 mL/min
FID - Air flow	~275 mL/min
- H_2 flow	~30 mL/min
Detector temperature	250°C

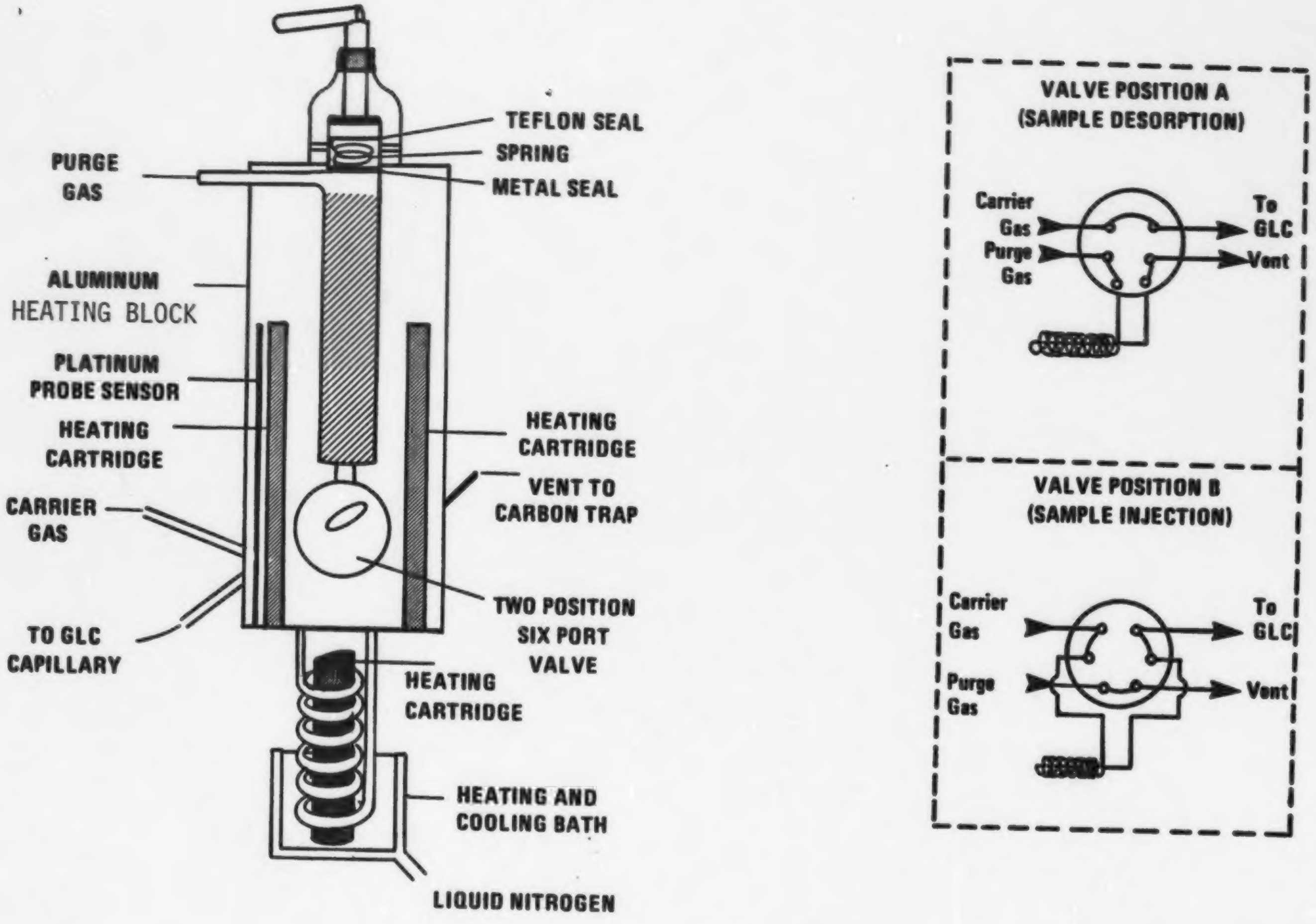
TEFLON SEAL
SPRING
METAL SEAL
PURGE GAS
ALUMINUM HEATING BLOCK
PLATINUM PROBE SENSOR
HEATING CARTRIDGE
CARRIER GAS
TO GLC CAPILLARY
HEATING CARTRIDGE
VENT TO CARBON TRAP
TWO POSITION SIX PORT VALVE
HEATING CARTRIDGE
HEATING AND COOLING BATH
LIQUID NITROGEN
VALVE POSITION A (SAMPLE DESORPTION)
Carrier Gas
Purge Gas
To GLC
Vent
VALVE POSITION B (SAMPLE INJECTION)
Carrier Gas
Purge Gas
To GLC
Vent

Figure 10. Inlet-manifold.

A Varian Model 3700 GC equipped with a thermal desorption inlet manifold (Fig. 10) and a Varian CDS 111 integrator was used to obtain chromatographic peak areas for each of the components in the mixture.

A GLC oven was used to heat the nickel cryogenic trap and transfer the vapors to Tenax® GC cartridges. This was accomplished as follows: the helium gas was set to pass at 200 mL/min through a transaxial trap submerged in liquid N_2 for cleaning the helium gas. Then this clean trap under He flow was placed in Dewar flask No. 1 and liquid nitrogen was slowly added until full and the system was equilibrated. The helium flow was then reduced to 20 mL/min. A second Dewar was filled halfway with finely crushed dry ice. The sample trap (which had been stored on dry ice) was immediately inserted and the Dewar No. 2 filled full of dry ice. After equilibration, the end cap (downstream) was removed and the Tenax® GC "transfer" cartridge was attached. The end cap (upstream) was removed and the stainless steel flex tube flowing with clean He (20 mL/min) was connected using a 0.25 in x 0.25 in stainless steel union. The trap was lifted from the second Dewar and placed across the open face of the GLC oven with the Tenax cartridge on the outside edge of the oven. The oven and therefore the trap was programmed from 30 to 160°C at 15°/min. The temperature was held at 160° for 2 min and then the Tenax cartridge was returned to the Kimax® culture tube. After the oven was cooled to room temperature, the downstream end cap was placed on the trap and then upstream was also capped. The analysis of the Tenax® GC transfer cartridges containing the content of the cryogenic traps was identical to the procedures described for Tenax GC sampling cartridges.

Calibration--For the analysis of Tenax® GC cartridges including vapors transferred from cryogenic traps, the thermal desorption/gas chromatography (TD/HRGC) data system was calibrated using two independent techniques. The first method utilized permeation tubes in a permeation system used specifically for calibrating instruments (8-10). This permeation system was not the one used in these studies. Quantities of each test compound were loaded onto Tenax GC cartridges as a group and then analyzed according to the conditions described in Table 8. Levels of the test compounds were loaded at several different levels and a linear regression analysis was made (calibration curve).

The second technique was used for verification of the first and employed the preparation of test compounds in a methanol solution and then injecting 2.0 μL into a flash (250°C) evaporation unit (Fig. 11). The components were swept by clean He (30 mL/min, 500 mL total volume) onto Tenax® GC cartridges. Subsequently, the cartridges were analyzed and the FID responses were measured by a Varian chromatography data system. Standard curves using linear regression analysis were prepared. The use of the flash evaporation unit was applicable to compounds with breakthrough volumes significantly larger than methanol (ca. 500 mL) and thus verification of standard curves for vinyl chloride, methyl chloride, acrylonitrile, furan and chloroprene were not possible by this procedure.

Charcoal Cartridges--

Recovery--The content of the charcoal sampling trap was emptied into a 1 mL volumetric flask and a carbon disulfide/methanol solution (30/70 v/v) was added to the mark. After 1 hr of desorption, aliquots were taken for gas chromatography analysis with flame ionization and electron capture detection (GC/FID and GC/ECD, respectively). Table 9 presents the operating parameters for the GC/FID and ECD. These conditions were found to be the most suitable for the test model compounds.

Calibration--Solutions of compounds for analysis by GC/FID and GC/ECD were prepared in carbon disulfide and carbon disulfide/methanol, respectively. Standard curves were prepared from four points (including zero) calibration data (triplicate analysis per point) using linear regression analysis. Microliter quantities were injected into the GC and peak heights or areas were determined for calculating quantities and recoveries.

Air/Vapor Generation Procedure

Storage-Stability Study--

The permeation/dilution system described in Section 5 was used for generating synthetic air/vapor mixtures. The list of 27 test compounds (Table 2) was divided into two major groups, so that each chemical could be resolved during instrumental analysis. The Groups I and II contained 15 and 13 compounds, respectively, with 1,2,3-trimethylbenzene included in each group.

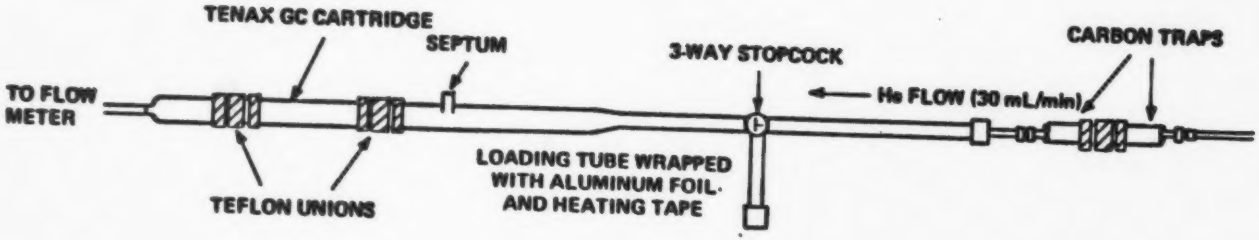
TENAX GC CARTRIDGE
SEPTUM
3-WAY STOPCOCK
CARBON TRAPS
TO FLOW METER
He FLOW (30 mL/min)
TEFLON UNIONS
LOADING TUBE WRAPPED WITH ALUMINUM FOIL AND HEATING TAPE

Figure 11. Schematic of vaporization unit for loading organics dissolved in methanol onto Tenax GC cartridges.

Table 9. OPERATING PARAMETERS FOR GC/FID AND GC/ECD ANALYSES OF SOLVENT DESORBED CHARCOAL TUBES

Parameter	Setting
GC/FID	
Injection port temperature	270°C
Detector temperature	270°C
Carrier flow (N_2)	20 mL/min
Hydrogen flow	~30 mL/min
Air flow	~270 mL/min
Column-programmed	8°C/min
GC/ECD	
Injector port temperature	270°C
Detector temperature (Sc-^{3}H)	300°C
Carrier flow (N_2)	20 mL/min
Pulse width	1.0 μSec
Pulse interval (adjustable)	25-1000 μSec
Column - Isothermal Step 1	150°C
- Step 2	100°C

Each chemical was placed in a permeation tube (see Section 7 for preparation and calibration) and constant permeation established at 30°C. The group of permeation tubes used in each experiment was placed in the permeation/dilution system and the system equilibrated overnight before initiating any sampling of synthetic air/vapor mixtures. The flow through the glass manifold on the permeation/dilution system was at 5 L/min, thus allowing for more than one collection device to be attached during the experiments. The temperature on the glass dilution bulbs and manifold assembly was maintained at 200°C ± 1°C. Dilutions of the synthetic air/vapor mixture was made to achieve the ppt range when low level studies were conducted.

The supporting performance data and quality control and assurance practices invoked on the permeation/dilution system are given in Section 7.

Containers were filled by attaching the empty polymeric bags directly to the manifold port or by using a metal bellows pump to fill and pressurize the bulbs. Stainless steel cannisters and glass bulbs were filled at a rate of 1 L/min and 300 mL/min, respectively. Each was pressurized to 15 psi.

Traps were sampled at 1 L/min for 30 min with a Nutech Model 220-A sampler attached downstream to the collection device, with the device attached to the manifold.

Table 1 gave the experimental conditions employed for the storage-stability study.

Interference Study--

In this study ozone, SO_2 and NO_x levels and relative humidity were varied while the sampling time, storage time, and concentration were held constant. The levels employed are given in Table 10. These concentrations reflect high and low ambient levels of O_3, NO_x and SO_2.

Preliminary Preparations--The portable permeation system was employed for the execution of the interference study. The entire system was operated at ambient pressure. All connections and other components were glass or Teflon®.

Clean air was humidified by passing it though a fritted bubbler containing water and then irradiated with ultraviolet light to generate ozone. The ozone/water vapor in air mixture was mixed with nitric oxide and sulfur dioxide from certified gas cylinders to generate the required concentrations

Table 10. CONCENTRATIONS OF INORGANIC GASES EMPLOYED IN INTERFERENCE STUDIES

Potential Interferent	Containers		Traps	
	High	Low	High	Low
Ozone	360[a]	75	380	60
NO_2	360	100	380	60
SO_2	200	10	190	12
H_2O	90% RH[b]	26% RH	90% RH	30% RH

[a] Values in ppb. Levels were determined with Bendix O_3 and NO_x monitors by measuring at the point of sampling from the permeation/dilution system.

[b] RH = relative humidity, measured with a YSI Dew Point Sensor.

of each component. The entire interference gas mixture was mixed with the model compounds in the clean air stream within a mixing bulb contained in the permeation/dilution system oven which was heated to approximately 200°C.

Zero air was sampled to determine "zero" settings on the Bendix NO_x and ozone monitors. A certified tank of NO (NBS standard) was used to calibrate the NO_x monitor. A known concentration of NO_x was delivered and the "span" settings of NO, NO_2, and NO_x were adjusted. In all cases, $NO + NO_2 = NO_x$. The concentrations delivered (600 ppb) was greater than the concentration to be used experimentally and the meter readings below 600 ppb were assumed to be linear. The ozone generator was then calibrated according to slide settings, the position of which determined exposure of the air to the UV light. In all cases, if NO was greater than ozone, then NO_2 equalled the inital ozone concentration. An audit (Section 7) was performed on the ozone monitor and the results agreed with the originally determined values.

A certified tank of SO_2 (NBS standard) was used to deliver a known concentration of SO_2 into the system.

During the experiments the relative humidity was monitored with a YSI Dew Point Sensor. Ozone and nitrogen dioxide concentrations were monitored with a Bendix ozone monitor. Ozone concentrations were measured directly whereas nitrogen dioxide concentrations were measured by the difference in ozone concentration after gas phase titration. Sulfur dioxide concentrations were not monitored.

Air/vapor mixtures were generated using the Group I and II model compounds. The organic vapor concentrations ranged from 1-100 ppb.

Containers--The sample containers for the high level interference study were filled after allowing the dilution system to equilibrate overnight. The "Summa" polished stainless steel cans were filled to a pressure of 15 psig by drawing sample at 1 L/min from the glass manifold through a metal bellows pump fitted with a flow restrictor on the pump outlet. The glass bulbs were filled to a pressure of 15 psig at a rate of 300 mL/min in the same manner. The Tedlar bags were filled by attaching them directly to the glass manifold. Three containers of each type were filled with sample.

One container of each type was filled from the permeation/dilution system after having removed the permeation tubes the night before and allowing only interferent gases to flow. These containers served as controls. The same procedure was used in filling the containers for the low level interference study.

Traps--Tenax GC cartridge and cryogenic trap sampling was conducted as described for the storage-stability study with a few modifications to the cryogenic procedure. The Ni traps were filled with clean glass beads and liquid oxygen was the cryogen in this study.

RESULTS

Special Bag Studies

Polymeric bags have been extensively used in the past as viable containers for captive air irradiations. Both Tedlar® (polyvinyl fluoride) and Teflon® (fluorinated ethene propene) transmit almost the full solar spectrum and are easily fabricated. While Tedlar® tends to be slightly sturdier than Teflon®, it has also been found to offgas hydrocarbons due to the solvent used in making the Tedlar® material (1). Teflon® bags do not suffer from this problem since solvents are not used in its manufacture. However, for both types of polymeric bags substances have been found to permeate through the film (17,18). It has also been observed that substantial bag-to-bag differences exist with Teflon® acquired from different manufacturing batches (18).

The initial studies using Group I compounds and bags yielded chromatograms such as those shown in Figures 12-15. While initial chromatograms of Tedlar® and Teflon® bag content indicated principally Group I compounds, the chromatograms became increasingly complex with time. This increasing contamination with time of the Tedlar® and Teflon® bags was thought to be due to a number of possible factors: (1) leaking bags; (2) offgassing from the polymeric film, or (3) diffusion of contaminants from ambient air into the bags.

Even though the objective of this program was to evaluate containers, under a directive, effort was devoted to determining whether the contamination with time of the polymeric bags was due to offgassing of the film, permeation of substances through the walls, leakage or a combination of factors.

All bags used in this study were first tested for leaks by filling them three-quarters of the way full with clean air and placing a light book on

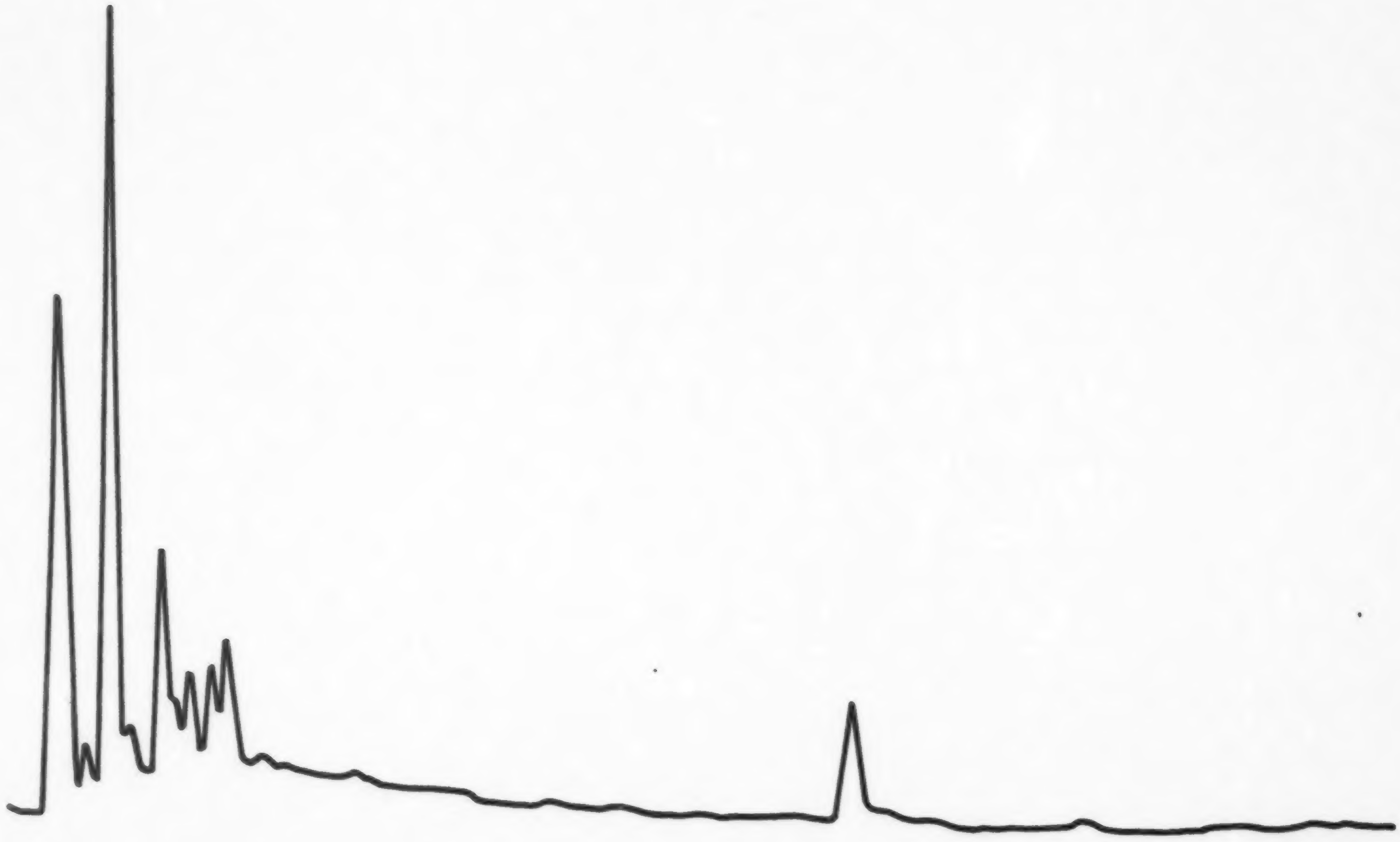

Figure 12. 2 mil Teflon Bag 61; low concentration study; Group I compounds; T_0, June 13, 1980.

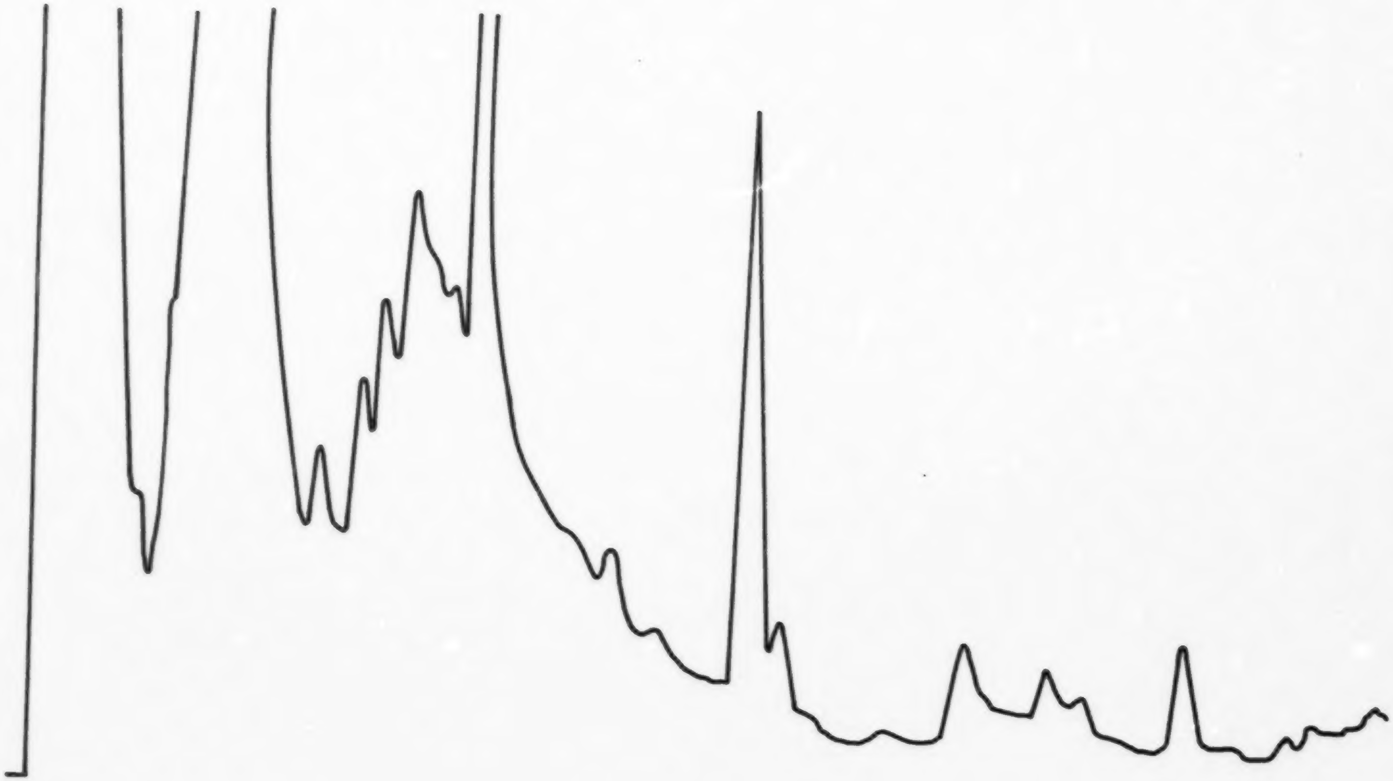

Figure 13. 2 mil Teflon Bag 61; low concentration study; Group I compounds; T_7, June 20, 1980.

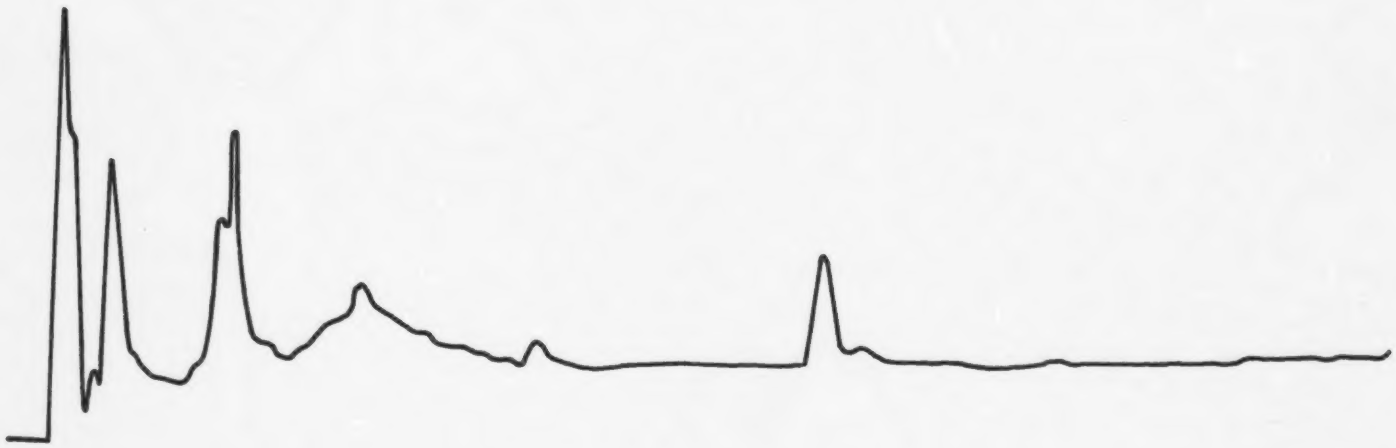

Figure 14. Tedlar Bag F; low concentration study; Group I compounds; T_0, June 5, 1980.

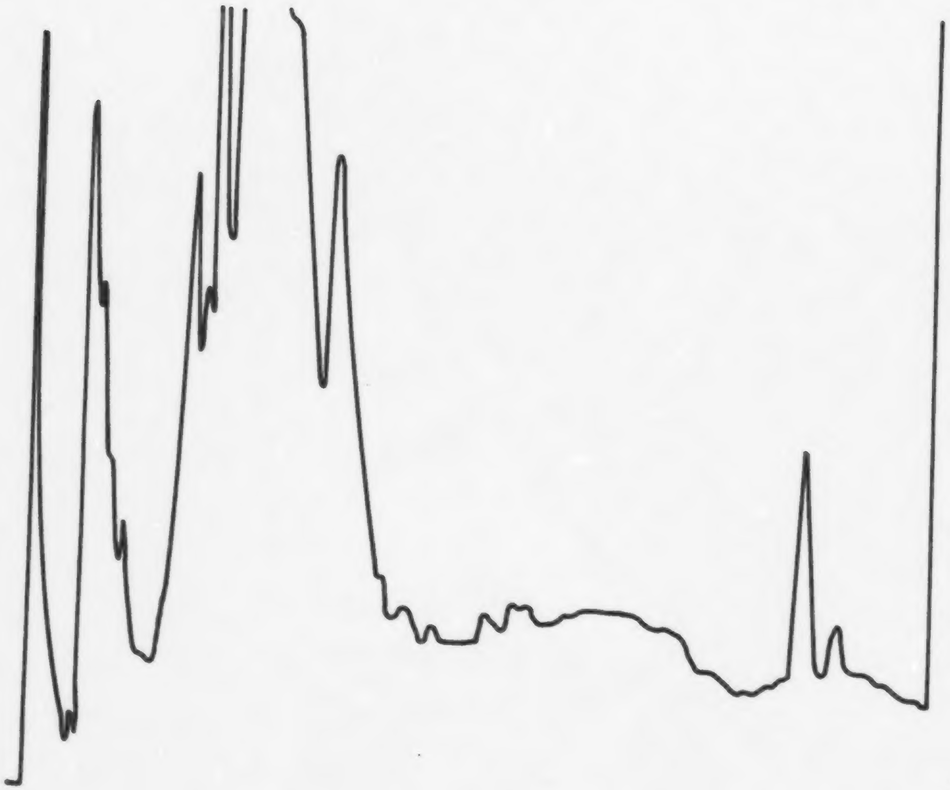

Figure 15. Tedlar Bag F; low concentration study; Group I compounds; T_7, June 12, 1980.

top. It should be noted that plastic bags are extremely fragile, especially Teflon®, so that care should be taken in the above procedure or the test itself may cause the bag to start leaking.

The bags were stored either in the lab inside an aluminum suitcase (to protect it from light) as in the low concentration study or inside a 3 ft x 2 ft x 1 ft steel box which was continuously flushed with clean air. The top of the box was equipped with a rubber gasket and the lid was held on with clamps so that the box remained air tight. A vacuum was held inside the box for several hours before use so it was considered acceptable for our purpose. It was decided to continually flush the box with clean air so that any leakage into the box or offgassing from the outside of the bags would be continually diluted instead of building up as in a static environment.

Several types of polymeric bags were used for the study. Five-layered, polyethylene/aluminized bags (Calibrated Instruments, Inc., Ardsley, NY) were tried but could not be cleaned sufficiently for use. Four Tedlar® bags, two which had been cleaned by irradiating at a high concentration of ozone and then flushed with clean air, and two new bags which had only been flushed once with clean air, were utilized for the actual studies. The type of cleaning treatment used may contribute to the amount of offgassing observed from the walls. Also, two types of Teflon® bags were used, three 2 mil and two 5 mil bags. If permeation plays a role in the contamination, then differences may be seen with film of different thicknesses.

Initial measurements of the bags containing clean air were taken as soon as the bags were filled. It took approximately one day for all bags to be filled and analyzed. An analysis was then taken seven days later, corresponding to the time span of the low concentration study, and then ten days later. Selected segments of example chromatograms taken on these days are shown in Figures 16-19. The segments shown are of the same time span so they can be compared quantitatively. This section of the chromatogram corresponds to the elution of lower molecular weight hydrocarbons (∿3 minutes to 10 minutes). The day initial measurements were taken, a contamination existed in our system which is the offscale peak shown in each chromatogram. This contamination did not exist on subsequent analysis days.

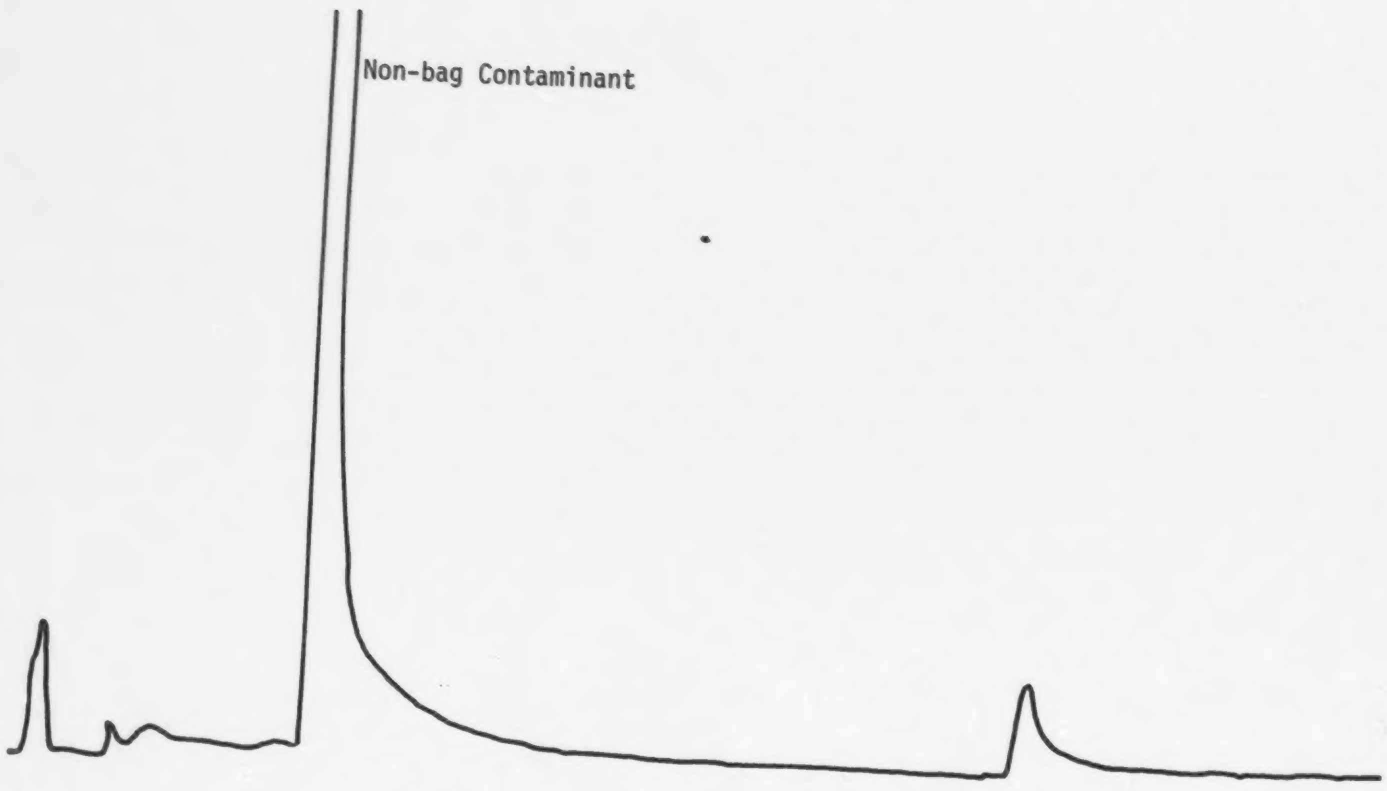

Figure 16. 2 mil Teflon Bag #61, zero air; bag stored in clean air; T_0, July 30, 1980.

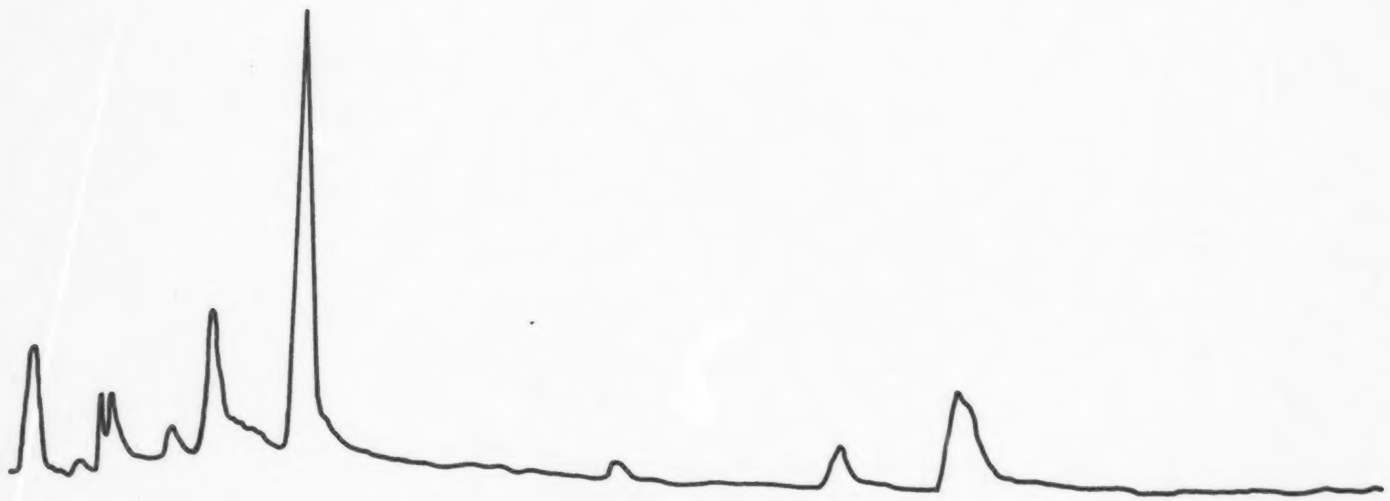

Figure 17. 2 mil Teflon Bag #61, zero air; bag stored in zero air; T_{10}, August 9, 1980.

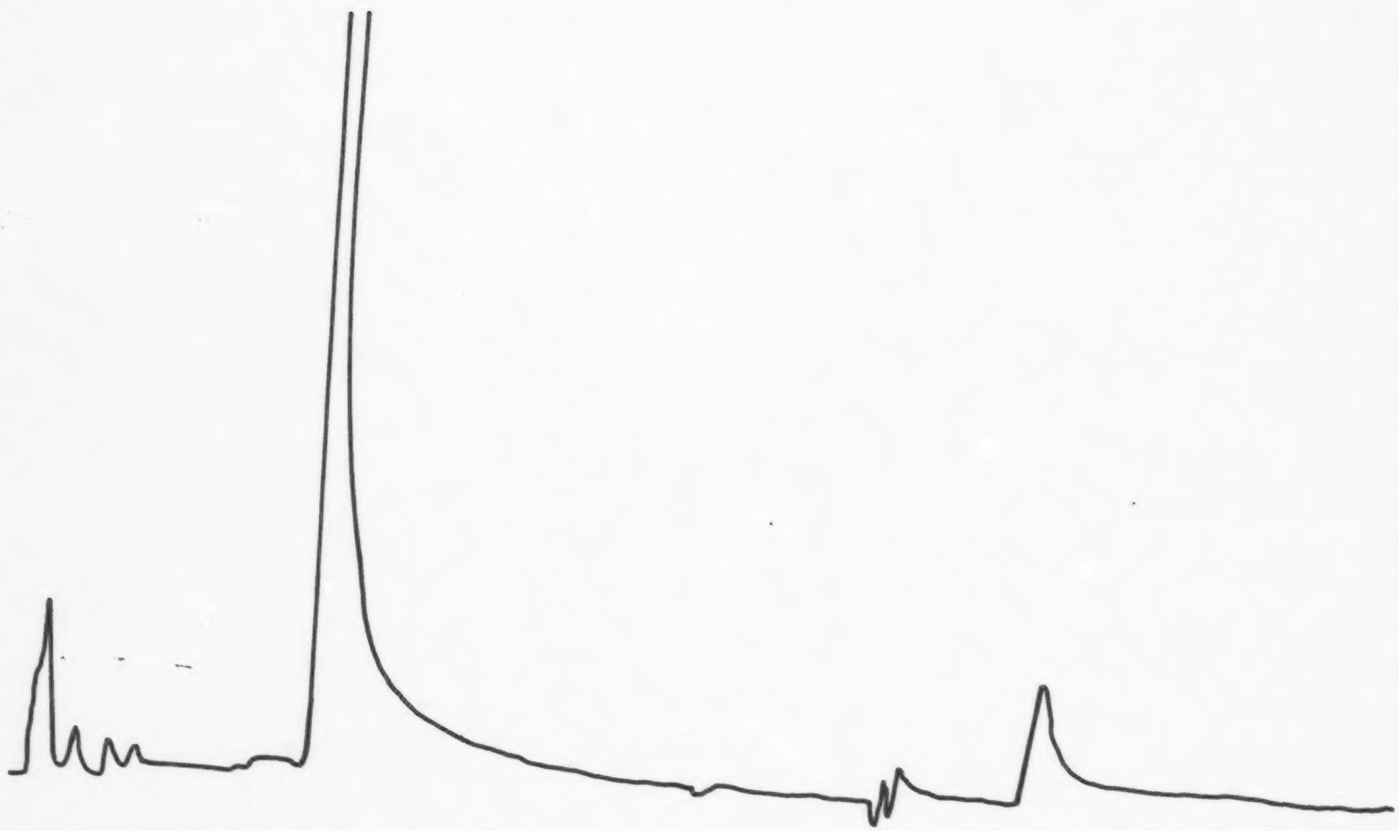

Figure 18. 2 mil Teflon Bag #62, zero air; stored in air lab; T_0, July 30, 1980.

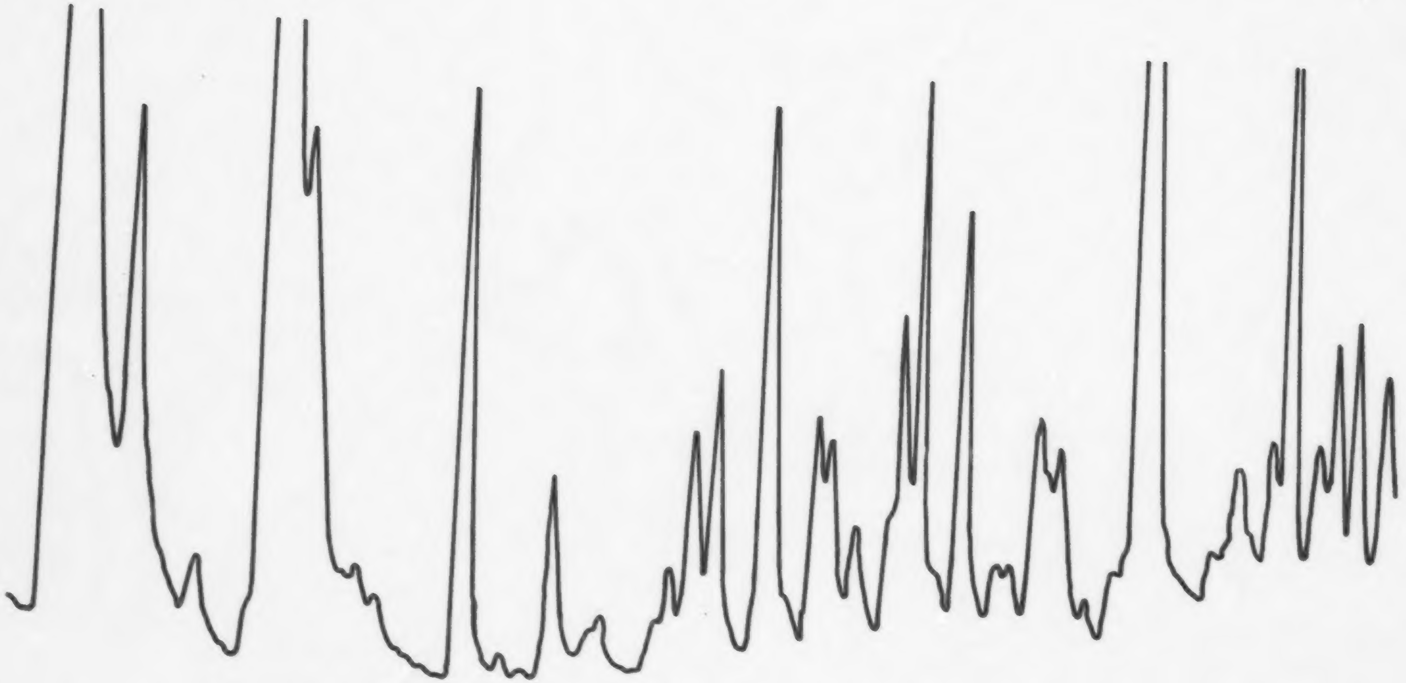

Figure 19. 2 mil Teflon Bag #62; zero air; stored in lab air; T_{10}, August 9, 1980.

As exemplified by these chromatograms, bags stored in ambient air contained considerably more contamination than those stored in a clean environment. Those stored in the clean air, however, did not remain entirely contamination free though the degree of contamination would not prevent their use in most sampling efforts. This could be due to several factors. The clean air bags were exposed to ambient air for short periods of time when analyses were being performed. It could be that this slight contamination is due to permeation of ambient air during these times. It also could be that contamination is due both to permeation and offgassing. The bags exposed to ambient air were stored in an aluminum suitcase. Only one type of bag was stored in each suitcase. If the bags offgassed, the immediate environment would be higher in hydrocarbons than the surrounding lab air. This may cause enhanced diffusion of hydrocarbons in to the bags and, therefore, explain some of the high levels of hydrocarbons measured in the bags. Support for this possibility comes from the Teflon® bags. Near the end of the chromatograms, where the higher molecular weight hydrocarbons elute, a number of peaks not observed with the Tedlar® bags occur in Teflon® bags exposed to ambient air and clean air. It is possible these peaks may be due to offgassing. While the quantity of these compounds is greater in the 2 mil exposed to ambient air as compared to the 2 mil in a clean environment, the quantities are close to equal in the two 5 mil Teflon® bags. This implies permeation also plays a role in this contamination. From our experiments offgassing appears to be indicated to some degree in both Tedlar® and Teflon® bags. Tedlar® seems to offgass in the lower molecular weight hydrocarbon region, while Teflon® appears to offgass higher molecular weight compounds. The different cleaning treatments of the Tedlar® bags appeared to make little or no difference in the amount of contamination observed with time.

The question arose as to whether or not different batches of Teflon® and Tedlar® would show different amounts of contamination with time. Thus a batch experiment was devised and carried out. Four Tedlar® and four Teflon® bags were used in the study with two bags of each film type coming from one batch and two bags of each film type coming from another batch.

After flushing each bag once with clean air, it was refilled with clean air and the air was analyzed. This constituted the day zero measurement.

For the purpose of gaining additional insight into the modes of bag contamination, one bag from each batch was stored in an aluminum case exposed to laboratory air while the other was stored in a steel box which was sealed and continually flushed with clean air. After storage for seven days in their respective environments, the bag contents were again analyzed.

An inter-batch comparison of areas at day zero is not justified since the bags would have been contaminated to different degrees during manufacture. A better comparison is the ratio of day 7 area to day 0 area for each bag. This accounts for any initial contamination while showing the offgassing and permeability properties of the bag. From Table 11, it can be seen that the Tedlar® bags in batch #2 had a greater increase in contamination than the Tedlar® bags in batch #1 in both environments. The Teflon® bags in batch #1 had a greater increase in contamination in both environments than those in batch #2.

The greater increase in total peak area for bags stored in the cases and exposed to laboratory air is not proof of permeation of gases through the bag wall, although data has previously been presented to suggest that permeation does play a significant role in contamination. Offgassing of material from the bag wall could give similar results. In the steel box flushed with clean air, gases coming off the outside bag wall would be removed. Gases coming off the inside bag wall could create a concentration gradient which would enhance permeation of gases out of the bag where they would be removed. Some offgassed material could still be detected if the rate of permeation and removal was not as great as the rate of offgassing. To test whether flushing with clean air enhanced loss of offgassed substances, and thus made permeation appear relatively more significant in laboratory-exposed bags, additional experiments were performed.

In the first experiment, three Teflon® bags were flushed three times with clean air, refilled with clean air, and the contents chromatographed. After analysis, all bags were placed in a steel box which had been purged overnight with clean air. The clean air purge was continued overnight to insure removal of contaminants. A chromatogram of the air in the steel box

Table 11. COMPARISON OF STORAGE ENVIRONMENT ON BAG BACKGROUND

Film Type	Batch #	Environment	Ratio of Total Area Counts Day 7/Day 0
Tedlar	1	Clean air	0.72
Tedlar	2	Clean air	2.30
Tedlar	1	Lab air	13.68
Tedlar	2	Lab air	20.33
Teflon	1	Clean air	16.60
Teflon	2	Clean air	3.64
Teflon	1	Lab air	40.40
Teflon	2	Lab air	7.26

on the morning of Day 1 revealed very little contamination compared to laboratory air.

On Day 3, the air in the steel box was again chromatographed to determine the extent of leakage and self-contamination. Subsequently, the contents of all 3 Teflon bags were chromatographed. Representative chromatograms from Days 0, 3, and 6 are shown in Figures 20-22 for the Teflon® bags; chromatograms of steel box, room air, and clean air are shown in Figures 23-26. The resulting peak areas are shown in Table 12.

To further test the mode of bag contamination, each Teflon® bag was stored in the laboratory air for an additional three days. The peak areas after laboratory storage are also shown in Table 12. The increase in total peak area between Day 0 and Day 3 can be attributed to leakage of room air into the steel box and/or offgassing from the walls of the box and permeation of these contaminants into the bag rather than offgassing within the bag. The much greater increase in total peak area after storage in laboratory air supports this idea since offgassing would not have been promoted simply by transfer of the bags to a laboratory air environment.

The second experiment was identical to the first except bags made from Tedlar® film were used in place of the Teflon®. Representative chromatograms from Day 0 and Day 3 are shown in Figures 27-32 along with chromatograms of room air, clean air, and steel box air. Total peak areas are shown in Table 13.

The contamination of air in the bags occurs principally by permeation of organic molecules through the bag walls. There is also a slight possibility that water molecules in large excess will displace organic molecules trapped within and on the bag walls. The extent of this displacement would be expected to be small however because of the hydrophobic nature of the Teflon® and Tedlar®. The possibility of this phenomenon is supported by these two studies since the air used to flush the steel box had been dried to some extent. Regardless, it appears that storage could be feasible if the bag environment is kept clean and relatively dry to prevent contamination.

Further support for the significance of the contribution of offgassed material to Teflon® bag contamination is given by Lonneman, et al. (19). Their study showed that heat pretreatment of Teflon® bags to 190°C was

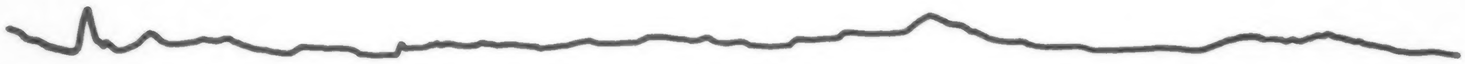

Figure 20. Chromatogram of air in Teflon® bag #13; T_0, December 16, 1980.

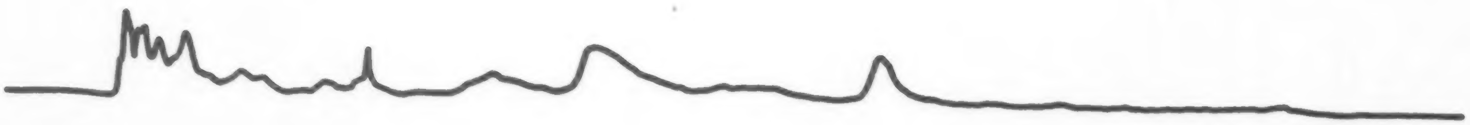

Figure 21. Chromatogram of air in Teflon® bag #13; T_3, December 19, 1980.

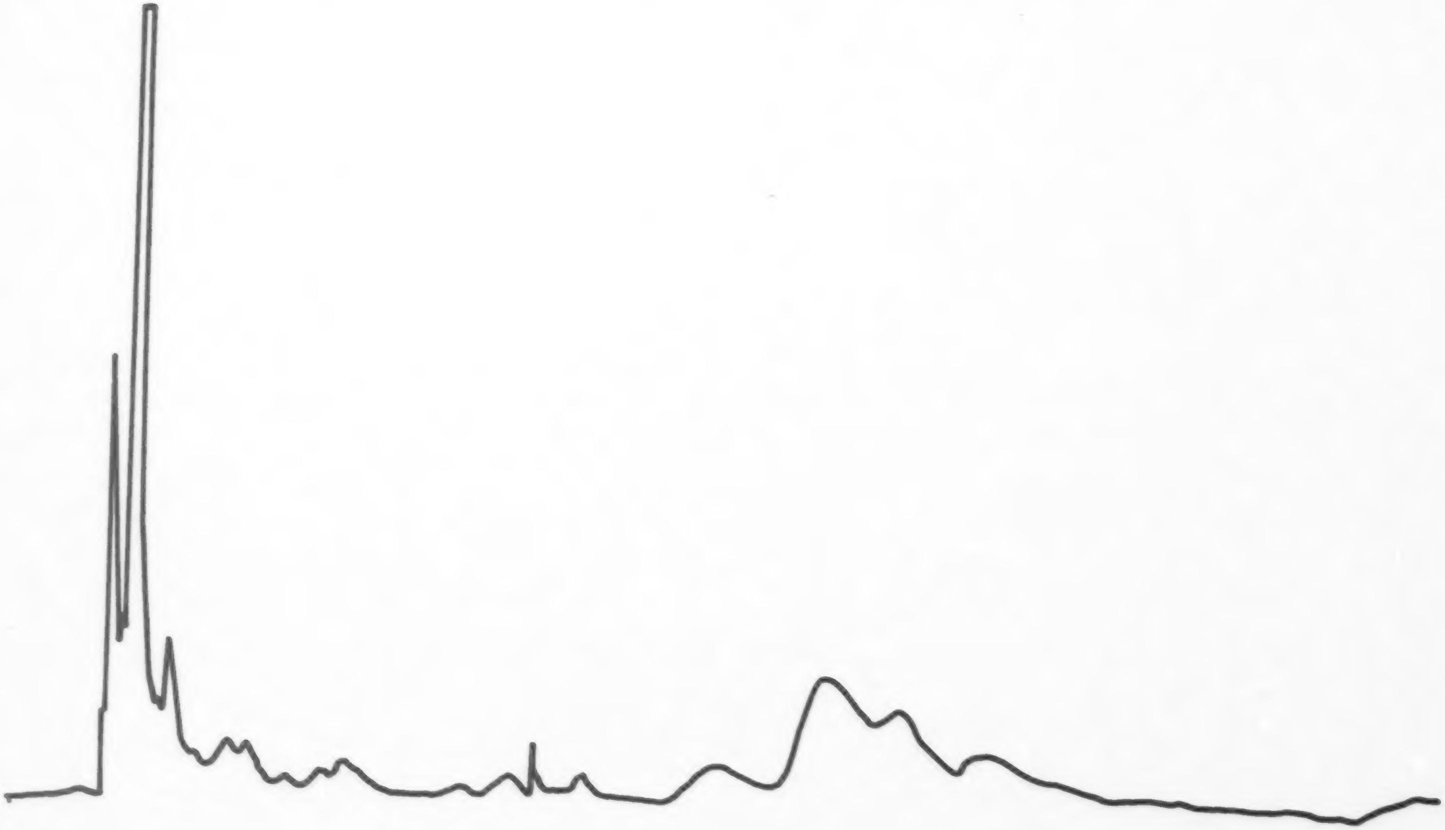

Figure 22. Chromatogram of air in Teflon® bag #13; T_6, December 22, 1980.

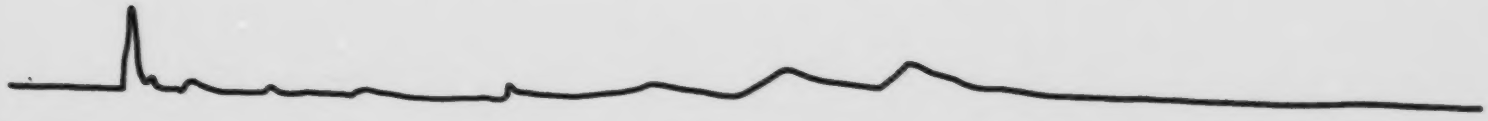

Figure 23. Chromatogram of air in steel box used for Teflon® bag experiment; T_1, December 17, 1980.

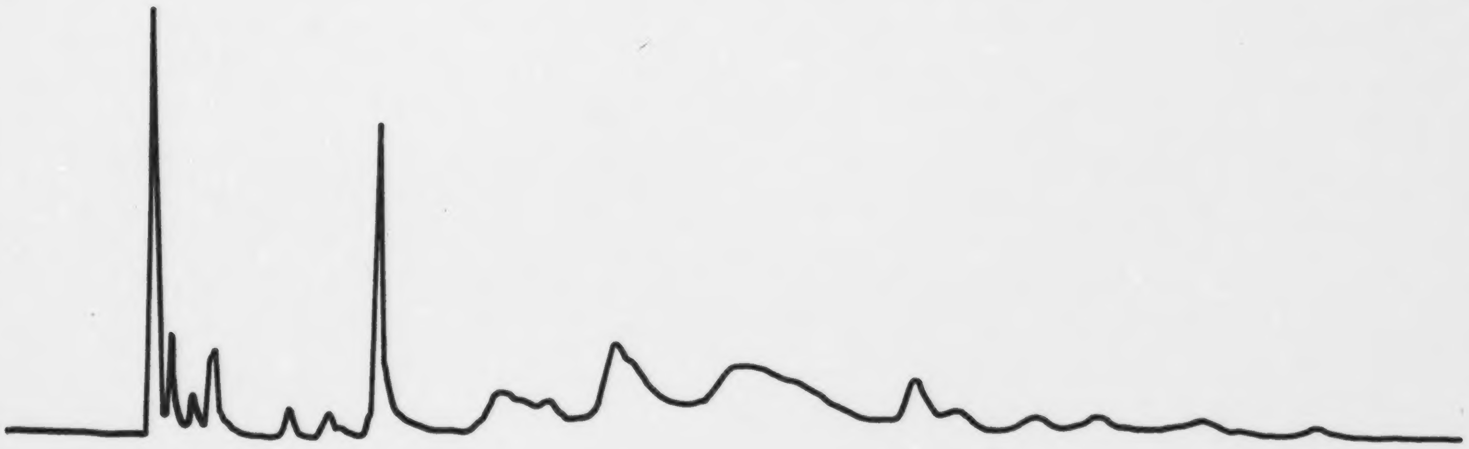

Figure 24. Chromatogram of laboratory air used for Teflon® bag experiment; December 16, 1980.

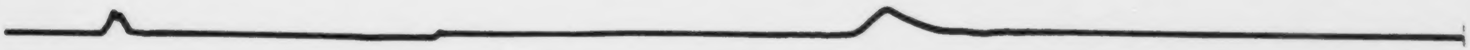

Figure 25. Chromatogram of clean air used for Teflon® bag experiment; T_0, December 16, 1980.

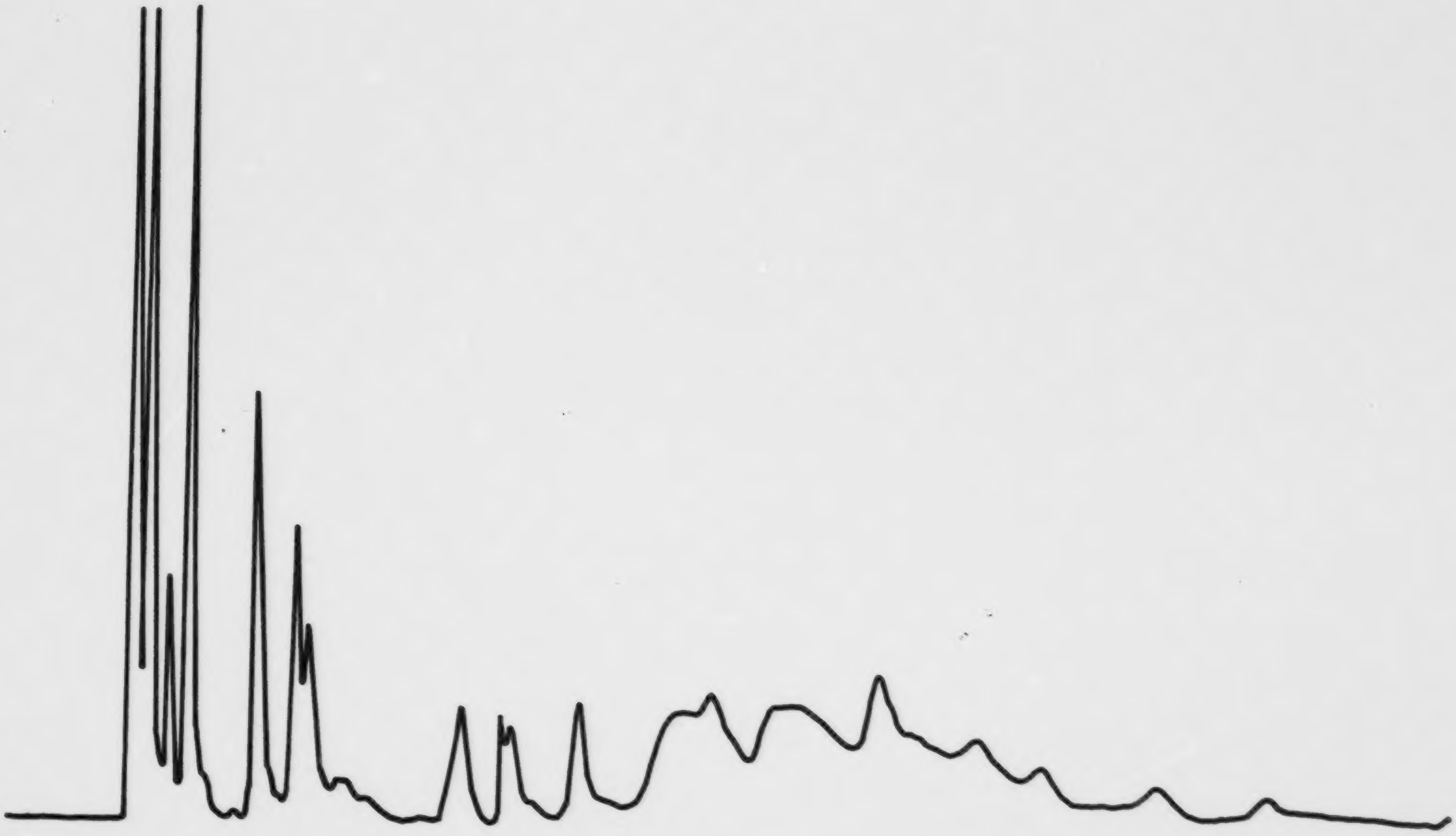

Figure 26. Chromatogram of air in steel box used for Teflon® bag experiment; T_3, December 19, 1980.

Table 12. EFFECT OF STORAGE ENVIRONMENT ON TEFLON® BAG BACKGROUND

Sample Source	Day 0	Day 3	Day 6[a]
Teflon® Bag #12	1028[b]	520	15,901
Teflon® Bag #13	367	2102	13,271
Teflon® Bag #14	371	2173	23,698
Steel Box	462	7300	-
Room Air	26,629	-	-
Clean Air	95	-	-

[a] Bags stored in lab air on days 4-6.

[b] Area in arbitrary units.

Table 13. EFFECT OF STORAGE ENVIRONMENT ON TEDLAR® BAG BACKGROUND

Sample Source	Day 0	Day 3
Tedlar Bag #7	342[a]	2648
Tedlar Bag #9	545	1150
Tedlar Bag #10	659	1423
Steel Box	438	14462
Room Air	20,278	--
Clean Air	162	--

[a] Area in arbitrary units.

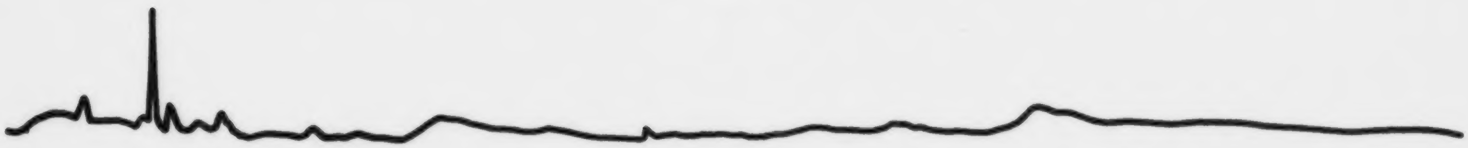

Figure 27. Chromatogram of air in Tedlar bag #IX; T_0, December 30, 1980.

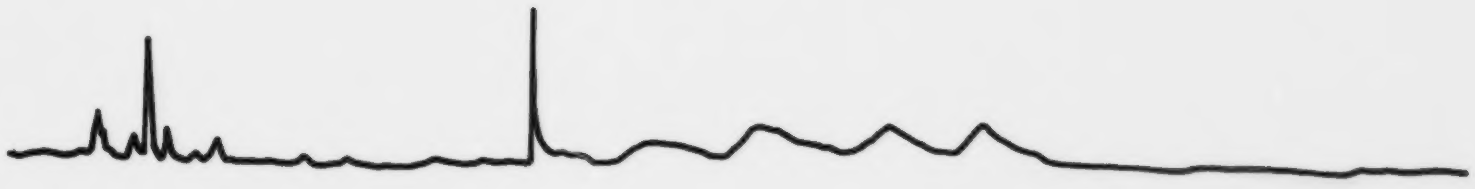

Figure 28. Chromatogram of air in Tedlar bag #IX; T_3, January 2, 1981.

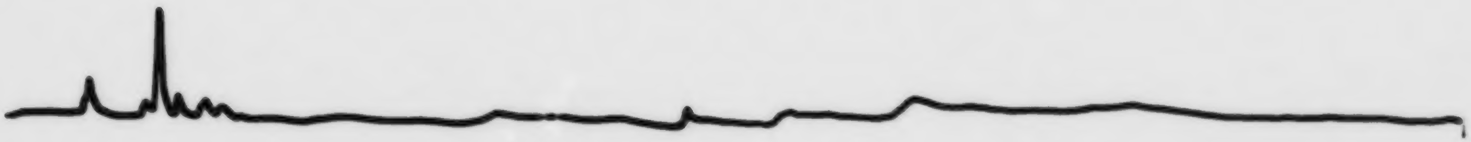

Figure 29. Chromatogram of clean air used for Tedlar® bag experiment; December 30, 1980.

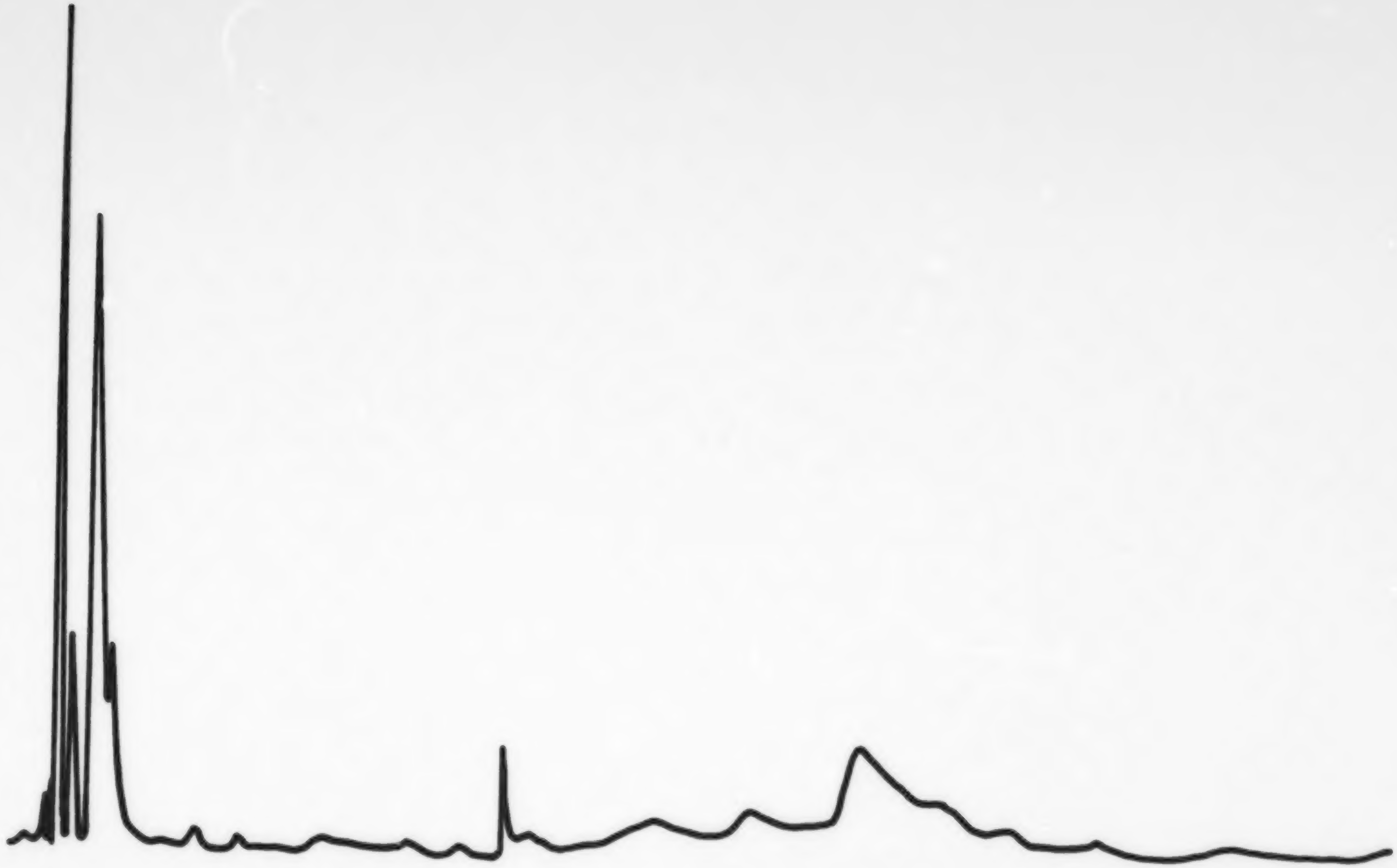

Figure 30. Chromatogram of air in steel box used for Tedlar® bag experiment; T_3, January 2, 1981.

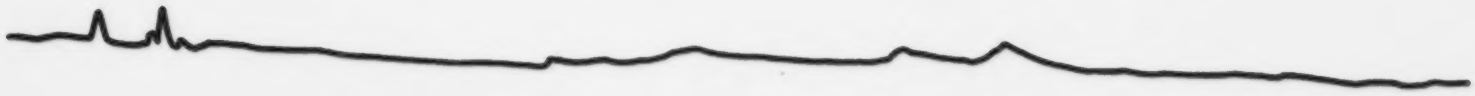

Figure 31. Chromatogram of air in steel box used for Tedlar® bag experiment; T_1, December 31, 1980.

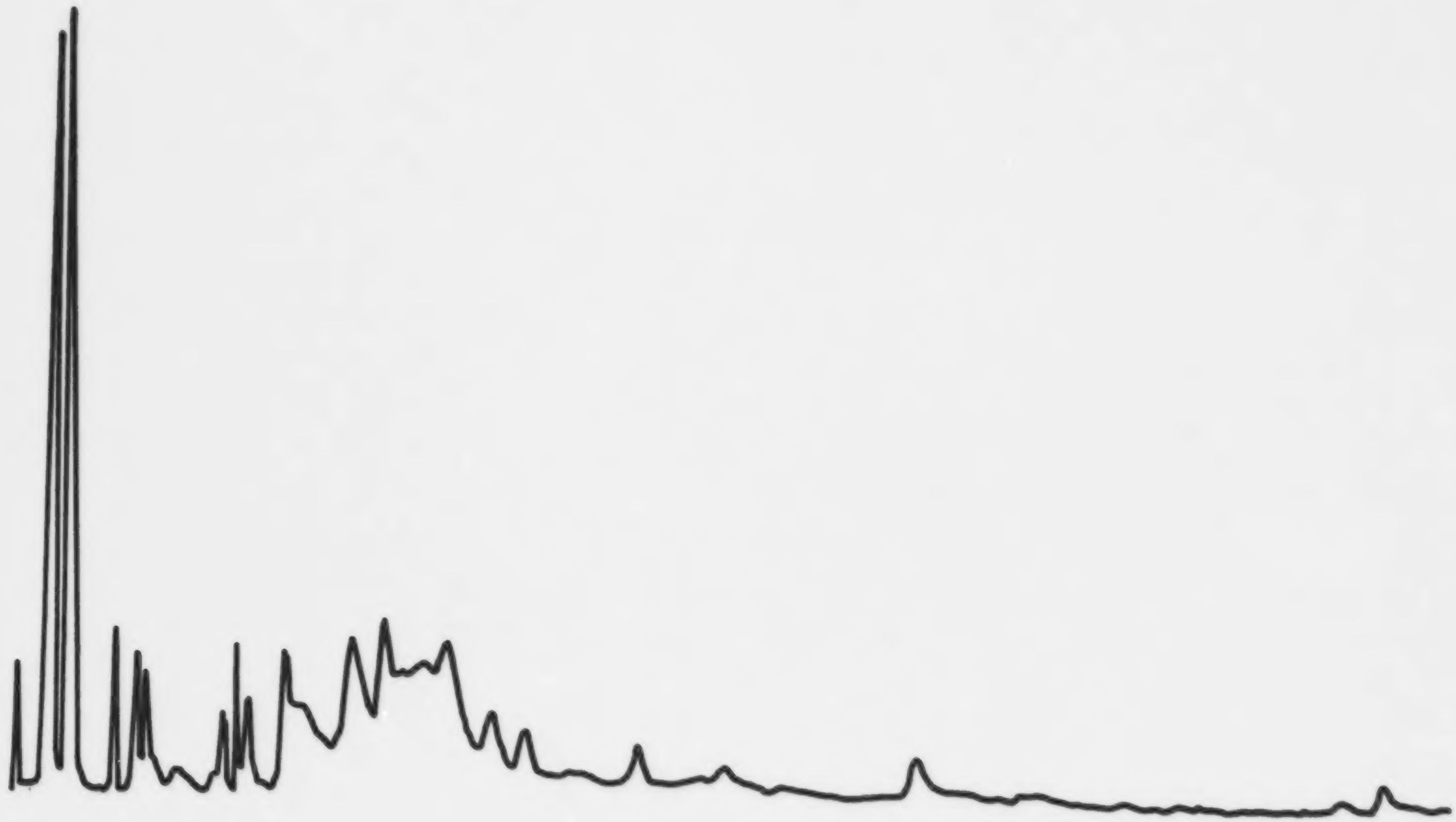

Figure 32. Chromatogram of laboratory air used for Tedlar® bag experiment; December 30, 1980.

necessary to prevent extensive offgassing but that the heavy molecular weight fraction was not affected as significantly as the low molecular fraction. Even after taking these measures, the contamination problem was not completely eliminated.

Regardless of the mode of contamination, storage of polymeric bags containing air samples in containers where the bag environment is contaminated is not acceptable if low level hydrocarbon measurements are to be made. The degree of contamination of polymeric bags also appears to be batch dependent.

It was decided that experiments with bags would be continued although these would involve only short-term storage of high concentration levels of test compounds in a "clean" environment.

Storage-Stability Studies

Containers--

Bags--Group I compounds were loaded into Teflon® and Tedlar® bags on January 8, 1981. The Teflon® bags were filled with about 10 liters of sample by attaching them directly to the glass manifold with a 1/4" Teflon® tube (Section 5, Figs. 1 and 3). The Tedlar® bags were filled with 20 liters of sample by the same method. Three bags of each type were filled with sample and one bag of each type was filled with clean air to serve as a control. The polymeric bags were stored in the steel box described previously. After placing the bags in the box, it was flushed with clean, dry air for about 20 hours and then sealed. The steel box was also flushed overnight after the Day 4 analyses to remove any laboratory air contamination which could have occurred during opening.

Analyses of the polymeric bags was performed on 0, 3 and 7 days of storage. (Day 0 analyses preceeded placing the bags in the steel box). Aliquots (200 mL) of the gas in each bag were taken into the cryogenic trap described previously without heating the bags. The cryogenically trapped organic compounds were then volatilized and measured using gas chromatography. The GC conditions are given in Table 14. The results of the analyses are shown on Tables 15 and 16. The recovery of the lower molecular weight compounds from Teflon® bags was highest on Day 0. The higher molecular weight compounds however, showed lower recoveries on Day 0, usually 70-80 percent. All compounds, excluding chloroprene and chloroform, showed large

Table 14. GC PARAMETERS FOR ANALYSIS OF CONTAINERS

Parameter	Setting/Conditions
Column	60 meter SCOT SE-30; 0.5 mm i.d.
Carrier gas	He 8 mL/min
Make-up gas	He 23 mL/min for FID
	5% CH_4 in Ar - 40 mL/min for ECD
Column temperature	4 min @ 30°C, 8°C/min, 2 min @ 185°C
FID - Air flow	40 psi
- H_2 flow	17 psi
GC	Perkin Elmer Model 3920
Detector temperature	200°C

Table 15. AVERAGE PERCENT RECOVERY OF GROUP I COMPOUNDS FROM TEFLON® BAGS

Compound	Ppb Sampled	Percent Recovery at Time[a]		
		T (0 days)	T (3 days)	T (7 days)
Vinyl chloride	28.6	95.5 ± 4.2 (4.4)	88.5 ± 5.2 (5.9)	79.4 ± 14.7 (18.5)
Methyl bromide	72.2	100.7 ± 0.8 (0.8)	84.1 ± 5.5 (6.6)	66.1 ± 14.4 (21.8)
Furan/acrylonitrile	142.8	99.2 ± 2.2 (2.3)	86.1 ± 5.3 (6.1)	69.3 ± 18.6 (26.8)
Chloroprene	5.2	84.6 ± 16.7 (19.8)	89.0 ± 25.6 (28.7)	136.5 ± 86.3 (63.3)
Chloroform	14.3	74.1 ± 5.6 (7.5)	500.6 ± 190 (38)	265.7 ± 189 (71)
Benzene	53.7	101.9 ± 10.8 (10.6)	81.9 ± 3.7 (4.5)	78.8 ± 15.5 (19.6)
1,2-Dichloropropane	25.2	37.7 ± 1.2	30.0 ± 0.0	31.0 ± 3.0
Toluene	22.7	85.0 ± 2.6 (3.0)	71.8 ± 2.6 (3.7)	64.8 ± 11.0 (16.9)
Tetrachloroethylene	27.7	79.4 ± 0.0 (0.0)	56.7 ± 2.2 (3.8)	49.5 ± 5.4 (10.9)
Chlorobenzene	15.9	75.5 ± 0.0 (0.0)	55.2 ± 2.2 (4.0)	44.0 ± 8.2 (18.7)
1,1,2,2-Tetrachloroethane	33.6	72.3 ± 1.8 (2.5)	72.3 ± 19.6 (27.2)	78.3 ± 30.1 (38.4)
m-Dichlorobenzene	18.5	70.3 ± 5.4 (7.7)	56.8 ± 16.8 (29.5)	67.0 ± 26.5 (39.5)
1,2,3-Trimethylbenzene	94.8	69.6 ± 1.1 (1.5)	48.2 ± 1.6 (3.3)	48.5 ± 2.1 (4.3)
Bis(2-chloroethyl)ether	19.3	72.5 ± 5.2 (7.1)	49.7 ± 8.5 (17.1)	36.3 ± 4.9 (13.6)

[a] Number in parenthesis is coefficient of variation.

Table 16. AVERAGE PERCENT RECOVERY OF GROUP I COMPOUNDS FROM TEDLAR BAGS

Compound	Ppb Sampled	Percent Recovery at Time[a]		
		T (0 days)	T (3 days)	T (7 days)
Vinyl chloride	28.6	98.9 ± 2.1 (2.1)	97.9 ± 5.9 (6.1)	110.3 ± 5.2 (5.2)
Methyl bromide	72.2	100.7 ± 2.1 (2.1)	97.9 ± 4.4 (4.5)	97.9 ± 5.8 (5.9)
Furan/acrylonitrile	142.8	100.4 ± 0.4 (0.4)	98.0 ± 4.9 (5.0)	98.9 ± 5.0 (5.1)
Chloroprene	5.2	100.0 ± 8.8 (8.8)	93.7 ± 4.0 (4.3)	467 ± 323 (69)
Chloroform	14.3	66.1 ± 1.5 (2.2)	473.4 ± 418 (86)	70.6 ± 6.9 (9.9)
Benzene	53.7	94.4 ± 3.9 (4.1)	94.9 ± 1.9 (1.9)	94.9 ± 6.7 (7.1)
1,2-Dichloropropane	25.2	31.7 ± 1.5[b]	33.0 ± 1.0[b]	33.0 ± 1.7[b]
Toluene	22.7	88.1 ± 0.0 (0.0)	82.4 ± 2.6 (3.2)	85.0 ± 5.3 (6.2)
Tetrachloroethylene	27.7	81.9 ± 2.2 (2.6)	78.3 ± 2.2 (2.8)	80.5 ± 4.3 (5.4)
Chlorobenzene	15.9	81.8 ± 0.0 (0.0)	71.1 ± 3.8 (5.3)	73.6 ± 3.8 (5.1)
1,1,2,2-Tetrachloroethane	33.6	72.3 ± 1.8 (2.5)	66.4 ± 1.8 (2.7)	67.6 ± 1.8 (2.6)
m-Dichlorobenzene	18.5	70.3 ± 0.0 (0.0)	63.2 ± 3.2 (3.2)	64.9 ± 5.4 (8.3)
1,2,3-Trimethylbenzene	94.8	71.4 ± 1.3 (1.8)	63.6 ± 0.6 (0.9)	66.8 ± 3.2 (4.7)
Bis(2-chloroethyl)ether	19.3	76.2 ± 3.1 (4.1)	58.5 ± 3.1 (5.3)	60.6 ± 3.1 (5.1)

[a] Number in parenthesis is coefficient of variation.

[b] Low recovery due possibly to variability/failure of permeation tube or system.

decreases in recovery from Day 0 to Day 7. Unknown interferences prevented quantitation of the chloroprene and chloroform. The extent of interference was variable and could not be accurately quantified by subtraction of the blank determined using the control bag. The large increase in the variability of the results on Day 7 indicates bag variability rather than measurement variability. There was a significant increase in the background levels in the control bag, even with storage in the clean atmosphere of the steel box. A contributing source of control bag background apparently is compound permeation out of the sample bags and into the control bag.

The recoveries from Tedlar® bags (Table 16) were generally higher than those with Teflon® both on Day 0 and Day 7. Also the recovery variability was much less with Tedlar® on Day 7. Interferences again prevented quantitation of chloroprene and chloroform.

A second group of compounds (Group II) was used for testing in June, 1981. The test samples were generated with the permeation/dilution system described earlier but which was modified for these measurements. The permeation rates were low for these compounds and thus extensive dilution was not necessary. The mixing bulbs were replaced with a straight, one-inch diameter glass pipe and dilution air was flowed directly across the permeation tubes to achieve below 100 ppb for each compound. This modification was also used in testing traps.

Of the polymeric bags only Tedlar® bags were tested with Group II compounds. Tedlar® was used as it showed better overall recovery and recovery precision than the Teflon®. Again the bags were filled directly from the manifold. All previous experiments indicated that the bags could only be used for storage for a short period of time unless they were maintained in a "zero air" environment. As a practical matter then, the Tedlar® bags were analyzed on Day 0 only and without storage, or within a matter of hours after they were filled; this was considered a realistic test of the usefulness of the bags. By applying the appropriate calibration factors, the ppb level of each compound in the bags on Day 0 was determined. The relative percent recovery was calculated from these measured ppb levels and the expected levels of each compound. These results are presented in Table 17. The best recovery was obtained with methyl chloride, vinylidene chloride and allyl

Table 17. PERCENT RECOVERY OF GROUP II COMPOUNDS FROM TEDLAR® BAGS

Compound	ppb Sampled	Percent Recovery (Day 0)[a]
Methyl chloride	56.6	83.3 ± 1.1 (1.3)
Methyl mercaptan	59.6	64.4[b]
Propylene oxide	27.6	Not detected
Vinylidene chloride	20.9	85.2 ± 5.7 (6.7)
Allyl chloride	91.4	100.3 ± 2.1 (2.1)
1,1,1-Trichloroethane	12.9	74.4 ± 6.2 (8.3)
α-Epichlorohydrin	67.2	Not detected
Ethylbenzene	7.5	88.0 ± 10.7 (12.2)
o-Xylene	21.2	34.4 ± 3.3 (9.6)[c]
n-Decane	7.8	76.9 ± 20.5 (26.6)
1,2,3-Trimethylbenzene	72.2	29.5 ± 1.5 (5.1)[c]
o-Cresol	21.4	Not detected
Nitrobenzene	27.2	65.8 ± 6.6 (10.0)

[a] Number in parenthesis is coefficient of variation.

[b] Single observation.

[c] Low recovery due possibly to variability/failure of permeation tube or system.

chloride. Propylene oxide and α-epichlorohydrin were not detected in the Tedlar® bags and only weakly and erratically detected as standards. o-Cresol was not detected in the Tedlar® bags or as a standard, possibly because of its boiling point which is 190.9°C.

Glass Bulbs--The two groups of compounds used to test Tedlar® bags were also used to test the glass bulbs. Each glass bulb was pressurized to about 10 psig by passing sample at a rate of 300 cc/minute through a metal bellows pump and into the bulb. The bulbs were stored in boxes to protect them from light. At the appropriate times, the samples were withdrawn from the bulbs with the bulbs at room temperature. The results of these analyses are shown in Table 18. Glass bulbs show a general decrease in recovery of compounds with increasing boiling point. A small decrease in recovery occurred generally from Day 0 to Day 3 and an increase occurred from Day 3 to Day 7. There is no ready explanation for this increase which occurred with the groups of compounds studied in January and June, respectively. One possibility though, is a relatively rapid loss of the organic compounds to the glass and then slow displacement from the glass by the small amount of water in the sample gas. A large interference was observed on some of the sample chromatograms of the first sample group on Days (3) and (7) between 5 and 15 minutes retention time. This interference, which prevented the measurement of the methyl mercaptan, was thought to be due to contamination from the o-rings to seal the Teflon® stopcocks.

Stainless Steel Cannisters--The two types of steel containers, electropolished and "Summa" polished, were tested with the first group of compounds whereas only the "Summa" polished containers were also tested with the second group of compounds. The electropolished containers were not included in the second test as they yielded recoveries similar to but not quite as good as those obtained with the "Summa" polished containers. A metal bellows pump which was used to fill the cans with sample was first equilibrated by drawing sample through it for several minutes. The pump outlet was then connected to the container valve and each container filled at a rate of 300 cc/min. The electropolished stainless steel cans were pressurized to 15 psig which corresponded to 4 liters of sample. The "Summa" polished cans were pressurized to 10 psig which corresponded to 12 liters of sample.

Table 18. PERCENT RECOVERY FROM GLASS BULBS

Compound	ppb Sampled	T_0 (0 days)^a	T_3 (3 days)^a	T_7 (7 days)^a
Methyl chloride	56.6	76.8 ± 3.0 (3.9)	74.5 ± 8.1 (10.9)	79.7 ± 7.6 (9.5)
Vinyl chloride	28.6	96.9 ± 2.1 (2.2)	95.5 ± 2.1 (2.2)	96.9 ± 2.1 (2.2)
Methyl bromide	72.2	98.8 ± 1.7 (1.7)	97.4 ± 0.8 (1.2)	98.8 ± 0.8 (0.8)
Methyl mercaptan	59.6		Interference - not detected	
Furan/acrylonitrile	142.8	97.8 ± 3.6 (3.7)	95.0 ± 1.1 (1.1)	99.2 ± 4.6 (4.6)
Propylene oxide	27.6		Not detected	
Vinylidene chloride	20.9	105.7 ± 18.7 (17.1)	100.9 ± 16.3 (16.2)	75.1 ± 13.4 (17.8)
Allyl chloride	91.4	92.3 ± 6.4 (6.9)	92.0 ± 6.4 (7.0)	96.1 ± 5.9 (6.1)
Chloroprene	5.2	94.2 ± 5.4 (5.7)	91.3 ± 4.0 (4.4)	91.3 ± 1.3 (1.4)
Chloroform	14.3	76.9 ± 0.0 (0.0)	69.9	69.9
1,1,1-Trichloroethane	12.9	65.9 ± 10.8 (16.4)	62.0 ± 7.8 (12.6)	68.2 ± 3.9 (5.7)
Benzene	53.7	87.5	81.9	83.8
1,2-Dichloropropane	25.2	34^b	34^b	32^b
Toluene	22.7	85.0 ± 2.6 (3.1)	83.7 ± 0.0 (0.0)	85.9 ± 3.1 (3.6)
α-Epichlorohydrin	67.2		Not detected	
Tetrachloroethylene	27.7	79.4 ± 0.0 (0.0)	78.3 ± 2.2 (2.8)	81.2 ± 2.5 (3.1)
Chlorobenzene	15.9	75.5 ± 0.0 (0.0)	75.5 ± 0.0 (0.0)	77.4 ± 3.8 (4.9)
Ethylbenzene	7.5	66.7 ± 1.3 (1.9)	65.3 ± 5.3 (8.1)	86.7 ± 8.0 (9.2)
o-Xylene	21.2	25.5 ± 1.9 (7.4)	24.0 ± 1.9 (7.9)	34.9 ± 4.7 (13.5)
1,1,2,2-Tetrachloroethane	33.6	66.4 ± 1.8 (2.7)	65.5 ± 0.0 (0.0)	69.3 ± 1.8 (2.6)
m-Dichlorobenzene	18.5	63.2 ± 3.2 (5.1)	63.2 ± 3.2 (5.1)	68.6 ± 3.2 (4.7)
n-Decane	7.8	51.3 ± 5.1 (9.9)	43.6 ± 3.8 (8.7)	64.1 ± 19.2 (30.0)
1,2,3-Trimethylbenzene	94.3	62.2 ± 2.1 (3.4)	60.2 ± 4.4 (7.4)	66.8 ± 3.2 (4.7)

(continued)

Table 18 (cont'd.)

Compound	ppb Sampled	T_0 (0 days)	T_3 (3 days)	T_7 (7 days)
Bis(2-chloroethyl)ether	19.3	79.3 ± 3.1 (3.9)	72.5 ± 0.0 (0.0)	77.7 ± 0.0 (0.0)
o-Cresol	21.4	Not detected		
Nitrobenzene	27.2	66.9 ± 9.2 (13.8)	61.4 ± 0.4 (0.6)	62.5 ± 0.4 (0.6)
Benzyl chloride	29.2	42.5 ± 3.4 (8.0)	37.7 ± 2.0 (5.3)	47.6 ± 6.2 (13.0)

[a] Number in parenthesis is coefficient of variation.

[b] Low recovery due possibly to variability/failure of permeation tube or system.

Three of each container type were filled with sample, and one of each type was filled with clean air to serve as a control. Analyses of each steel container involved placing the container in the small oven described previously and heating it to ~90°C for at least 5 minutes prior to sample removal. As with the other containers, 200 mL of sample was taken for each measurement.

The percent recovery for Group I compounds from the electropolished containers is presented in Table 19. The percent recovery decreases with increase in boiling point. The low boiling compounds show a modest loss in recovery with time while the high boiling compounds generally show a drop in recovery from Day 0 to Day 3 and then a leveling off in recovery. Two compounds which produced inconsistent results with variation in the boiling point were 1,2-dichloropropane and bis-(2-chloroethyl)ether. The low recovery of the former and high recovery of the latter could have been due to a change in the permeation tubes occuring between filling the containers and calibration of the detector response.

The recovery values for the "Summa" polished containers are presented in Table 20. As with the electropolished container, recovery generally decreases with increase in boiling point. Also there is generally a decrease in recovery from Day 0 to Day 3 but no analytically meaningful change in recovery from Day 3 to Day 7 for a majority of the compounds.

As with the glass bulbs, recovery of some of the compounds was higher on Day 7 than on Day 3 or Day 0. One possible explanation for this is that the "Summa" cans were heated for a longer period of time on Day 7 than on either Day 3 or Day 0 before beginning to trap-out a sample. The average heating time on Day 0 was five minutes, on Day 3 was 20 minutes, and on Day 7 was 30 minutes. This could have lead to a greater fraction of the compounds being desorbed from the can wall on Day 7. Even though this variance in heating time was unintentional, some useful information may have been revealed. The "instability" of many compounds may not be a decomposition with irreversible loss but only the adsorption of the compounds on a cold surface. Complete recovery of these compounds may be possible by heating the container to a sufficient temperature to promote desorption but not thermal decomposition.

Table 19. RELATIVE PERCENT RECOVERY FROM ELECTROPOLISHED STEEL CONTAINERS

Compound	Ppb Sampled	Percent Recovery at Time[a]		
		T (0 days)	T (3 days)	T (7 days)
Vinyl chloride	30.9	98.1 ± 1.9 (1.9)	96.1 ± 1.9 (2.0)	94.8 ± 6.8 (7.2)
Methyl bromide	78.3	93.6 ± 3.8 (4.1)	91.1 ± 8.2 (8.9)	85.6 ± 7.2 (8.4)
Furan/acrylonitrile	154.9	93.6 ± 4.8 (5.2)	89.3 ± 6.9 (7.7)	81.9 ± 9.7 (11.8)
Chloroprene	5.65	87.3 ± 5.3 (6.1)	77.9 ± 10.8 (13.9)	69.6 ± 5.7 (8.1)
Chloroform	15.5	66.5 ± 3.9 (5.8)	70.9 ± 0.0 (0.0)	70.3 ± 11.6 (16.5)
Benzene	58.3	96.6 ± 6.5 (6.7)	89.2 ± 2.9 (3.3)	93.8 ± 10.5 (11.2)
1,2-Dichloropropane	27.2	57.0 ± 4.4[b]	55.3 ± 3.0[b]	57.0 ± 7.0[b]
Toluene	24.2	86.6 ± 2.4 (2.8)	82.5 ± 4.9 (5.9)	84.1 ± 6.1 (7.3)
Tetrachloroethylene	30.1	93.0 ± 6.6 (7.1)	92.0 ± 4.9 (5.4)	94.0 ± 15.6 (16.6)
Chlorobenzene	17.3	86.7 ± 0.0 (0.0)	80.9 ± 0.0 (0.0)	86.7 ± 9.8 (11.3)
1,1,2,2-Tetrachloroethane	36.4	49.2 ± 25.3 (51.4)	41.8 ± 26.4 (63.1)	37.1 ± 25.0 (67.4)
m-Dichlorobenzene	20.0	46.9 ± 21.9 (46.7)	38.2 ± 14.9 (39.1)	35.5 ± 10.5 (29.6)
1,2,3-Trimethylbenzene	102.9	44.9 ± 22.7 (50.6)	38.2 ± 15.8 (41.5)	36.2 ± 6.9 (19.1)
Bis(2-chloroethyl)ether	20.9	81.3 ± 19.1 (23.5)	79.9 ± 13.9 (17.4)	87.6 ± 7.2 (8.2)

[a] Number in parenthesis is coefficient of variation.

[b] Low recovery due possibly to variation/failure in permeation tube or system.

Table 20. RELATIVE PERCENT RECOVERY FROM SUMMA POLISHED STEEL CONTAINERS

Compound	Ppb Sampled	Percent Recovery at Time[a]		
		T (0 days)	T (3 days)	T (7 days)
Methyl chloride	56.6	81.4 ± 6.4 (7.9)	83.2 ± 3.9 (4.7)	78.1 ± 27.2 (34.8)
Vinyl chloride	30.9	101.3 ± 1.9 (1.9)	97.1 ± 0.0 (0.0)	98.1 ± 1.9 (2.0)
Methyl bromide	78.3	99.6 ± 0.0 (0.0)	95.4 ± 0.8 (0.1)	97.4 ± 1.5 (1.6)
Methyl mercaptan	59.6	50.0	40.7[a]	58.8 ± 24.7 (50.6)
Furan/acrylonitrile	154.9	97.9 ± 3.9 (4.0)	89.1 ± 3.6 (4.1)	86.7 ± 5.6 (6.4)
Propylene oxide	27.6		Not detected	
Vinylidene chloride	20.9	125.4 ± 21.5 (17.1)	119.6 ± 6.7 (5.6)	113.9 ± 45.9 (40.3)
Allyl chloride	91.4	97.7 ± 7.6 (7.8)	97.7 ± 7.8 (8.0)	98.8 ± 7.2 (7.3)
Chloroprene	5.65	95.0 ± 3.7 (3.9)	83.7 ± 5.1 (6.1)	81.9 ± 6.2 (7.6)
Chloroform	15.5	72.9 ± 3.9 (5.3)	70.9 ± 0.0 (0.0)	75.5 ± 3.9 (5.1)
1,1,1-Trichloroethane	12.9	69.0 ± 2.3 (3.3)	69.8 ± 7.0 (10.0)	74.4 ± 2.3 (3.1)
Benzene	58.3	97.8 ± 7.9 (8.1)	90.4 ± 2.6 (2.8)	95.5 ± 6.9 (7.2)
1,2-Dichloropropane	27.3	51.0 ± 4.4[c]	45.7 ± 5.7[c]	52.7 ± 3.2[c]
Toluene	24.6	90.7 ± 2.4 (2.7)	85.4 ± 4.1 (4.8)	88.2 ± 4.9 (5.5)
m-Epichlorohydrin	67.2		Not detected	
Tetrachloroethylene	30.1	90.7 ± 4.9 (5.5)	87.4 ± 4.9 (5.7)	89.7 ± 5.6 (6.3)
Chlorobenzene	17.3	90.8 ± 6.9 (7.6)	86.7 ± 5.8 (6.7)	88.4 ± 8.7 (9.8)
Ethylbenzene	6.5	80.0 ± 4.0 (5.0)	80.0 ± 12.0 (15.0)	94.7 ± 8.0 (7.8)
o-Xylene	21.2	34.4 ± 1.4 (4.1)	34.0 ± 5.2 (15.3)	41.5 ± 2.8 (6.7)
1,1,2,2-Tetrachloroethane	36.4	75 ± 1.6 (2.2)	69.5 ± 3.3 (4.7)	72.3 ± 4.1 (5.7)
m-Dichlorobenzene	20.0	71.5 ± 3.0 (4.2)	60.0 ± 5.0 (8.3)	56.0 ± 7.0 (12.5)
n-Decane	7.8	102.6 ± 15.4 (15.0)	79.5 ± 5.1 (6.4)	96.2 ± 16.7 (17.4)
1,2,3-Trimethylbenzene	72.2	93.5 ± 15.2 (16.2)	70.9 ± 8.4 (11.8)	89.7 ± 22.2 (24.7)

(continued)

Table 20 (cont'd.)

Compound	Ppb Sampled	Percent Recovery at Time		
		T (0 days)	T (3 days)	T (7 days)
Bis(2-chloroethyl)ether	20.9	106.7 ± 11.0 (10.3)	99.0 ± 10.0 (10.1)	101.9 ± 11.0 (10.8)
o-Cresol	21.4	Not detected		
Nitrobenzene	27.2	123.2 ± 43.8 (35.6)	103.3 ± 15.8 (15.3)	124.3 ± 48.0 (38.6)
Benzyl chloride	29.2	41.4 ± 12.0 (29.0)	Not detected	Not detected

[a] Number in parenthesis is coefficient of variation.

[b] Single observation.

[c] Low recovery is due possibly to variation/failure of permeation tube.

Traps--

The test parameters employed for the storage-stability study are given in Table 21. The sampling volume (30 L) and the relative humidity (30%) were held constant. No ozone, NO_x or SO_2 were added. The variable parameters were the concentration of each individual substance and storage time. Sampling rate and time were held constant throughout all of the experiments.

All sampling devices were evaluated simultaneously by sampling the air/vapor mixture concurrently to eliminate possible variability in the performance of the permeation/dilution system.

Tables 22 and 23 present the concentrations and the total quantity of the test compounds which were delivered to the sampling devices. The levels in ppb, total weight (ng), and the breakthrough volumes (Table 22) for these compounds on Tenax GC cartridges are indicated. The range of concentrations were 15-100 ppb and 2-858 ppt for the high and low level studies, respectively. The total quantity delivered to the sampling devices was based upon sampling 30 L of the air-vapor mixture from the permeation/dilution system.

Tenax GC Cartridges--The storage-stability study using Tenax GC cartridges was conducted according to the experimental design described above. Triplicate samples were collected for each experimental parameter (variable). All samples and blanks were collected during T_0 (T_0 = 0 day of storage study). Analysis of T_0 samples was performed within three hours of collection.

The absolute areas which were obtained for the samples analyzed at T_0, T_3 and T_7 were used to obtain the quantity of the material recovered by interpolation from calibration curves [response (area) vs. quantity]. Using the quantity (nanograms) of the material measured on the sampling cartridge the percent recovery was calculated as a ratio of observed to expected times 100.

The results for high and low level storage-stability are given in Tables 24 and 25, respectively.

All compounds were detected in the high level study (Table 24). Quantitative recoveries were observed for most compounds that had breakthrough volumes greater than the sample volume (30 L). The apparent lower recovery of benzene is probably due to an uncertainty in the initial instrument calibration, since subsequent studies have shown recoveries at least 25%

Table 21. TEST PARAMETER RELATIONSHIPS FOR EVALUATION OF TRAP TYPE COLLECTION DEVICES - STORAGE/STABILITY STUDY

Constant Parameters	Variable Parameters
Volume - 30 ℓ	Concentration - ppt and ppb
RH - 30%	Storage time (da) - t_0, t_3, t_7
$[O_3] = 0$	
$[NO_x] = 0$	
$[SO_2] = 0$	

Table 22. CONCENTRATIONS (HIGH LEVEL STUDY) AND TOTAL QUANTITY OF GROUP I COMPOUNDS DELIVERED TO SAMPLING DEVICES: TENAX GC, CHARCOAL, AND CRYOGENIC TRAPS

Compound	Concentration (ppb)	Total Wght. Delivered (ng)	Breakthrough Volume (ℓ)[a] (@80°F)
Vinyl chloride	48	3,672	1.0
Methyl bromide	80	5,587	1.0
Acrylonitrile	93	6,054	5
Furan	100	8,340	3
Chloroprene	4.5	487	15
Chloroform	15	2,196	18
Benzene	60	5,742	38
1,2-Dichloropropane	24	3,326	81
Toluene	24	2,714	173
Tetrachloroethylene	30	6,102	144
1,1,2,2-Tetrachloroethane	41	8,438	173
Chlorobenzene	17	2,346	344
Bis-(2-chloroethyl)ether	48	8,410	234
m-Dichlorobenzene	20	3,606	948

[a] On standard Tenax GC cartridge.

Table 23. CONCENTRATIONS (LOW LEVEL STUDY) AND TOTAL QUANTITY OF GROUP I COMPOUNDS DELIVERED TO SAMPLING DEVICES: TENAX GC, CHARCOAL, AND CRYOGENIC TRAPS

Compound	Concentration (ppt)	Total Wght. Delivered (ng)	Concentration (pg/L)
Vinyl chloride	17	13	428
Methyl bromide	429	50	1,675
Furan	542	46	1,517
Acrylonitrile	858	57	1,887
Chloroprene	2	2	57
Chloroform	82	12	400
Benzene	328	32	1,050
1,2-Dichloropropane	184	25	845
Toluene	132	15	502
Tetrachloroethylene	161	33	1,095
Chlorobenzene	95	13	437
1,1,2,2-Tetrachloroethane	351	73	2,420
Bis-(2-chloroethyl)ether	252	44	1,460
m-Dichlorobenzene	122	22	735

Table 24. PERCENT RECOVERY FOR HIGH LEVELS OF TEST COMPOUNDS FROM TENAX GC CARTRIDGES - WITH CORRECTION FOR BREAKTHROUGH VOLUME

Compound	B.P. (°C)	Breakthrough Volume (L)	ppb Sampled	Expected Quantity (ng/cartridge)	Storage Period		
					T_0 = 0 da	T_3 = 3 da	T_7 = 7 da
Methyl chloride	-24.2	3	56.3	3,480	9.7 ± 3.5 (36)	7.3 ± 2.4 (33)	6.6 ± 3.7 (56)
Vinyl chloride	-13	1	48	122	52 ± 29 (58)[a]	41 ± 7 (17)	50 ± 7 (14)
Methyl bromide	3.4	1	80	186	51 ± 7 (14)	63 ± 7 (11)	79 ± 2 (3)
Methyl mercaptan	6.2	-	60.2	3,548	9.0 ± 1.7 (19)	11.8 ± 8.5 (71)	6.7 ± 2.6 (38)
Furan	31.4	3	100	1,009	90 ± 8 (8)	89 ± 23 (26)	89 ± 36 (40)
Propylene oxide	34.3	4	27.6	1,965	46 ± 15 (32)	44 ± 5.9 (13)	41 ± 7.8 (19)
Acrylonitrile		5	93	834	112 ± 12 (15)	142 ± 19 (13)	165 ± 18 (11)
Vinylidene chloride	37	1	20.7	2,452	112 ± 18 (16)	174 ± 4.5 (3)	105 ± 26 (24)
Allyl chloride	45	6	93.4	8,752	17.4 ± 2.6 (15)	19.6 ± 6.4 (32)	19.5 ± 4.0 (20)
Chloroprene	59.4	15	4.5	243	80 ± 12 (15)	83 ± 1 (1)	88 ± 3 (3)
Chloroform	61.7	18	15	1,318	111 ± 21 (19)	139 ± 36 (26)	142 ± 29 (20)
1,1,1-Trichloroethane	74.1	9	13.4	2,182	23 ± 3.4 (15)	26 ± 10 (39)	23 ± 1.4 (6)
Benzene	77	38	60		65 ± 9 (14)	63 ± 9 (14)	71 ± 3 (4)
1,2-Dichloropropane	96.4	81	24	3,326	101 ± 14 (14)	99 ± 9 (9)	113 ± 6 (6)
Toluene	110.6	173	24	2,714	91 ± 10 (11)	89 ± 10 (12)	95 ± 2 (2)
α-Epichlorohydrin	116.5	54	38.3	4,335	67 ± 5.5 (8.2)	55 ± 6.1 (11)	59 ± 9.8 (16)
Tetrachloroethylene	121	380	30	6,102	97 ± 7 (7)	95 ± 13 (14)	96 ± 4 (4)
Chlorobenzene	132	344	17	2,346	105 ± 7 (7)	104 ± 8 (8)	106 ± 2 (2)
Ethylbenzene	136.2	344	7.4	968	88 ± 13 (15)	88 ± 12 (14)	89 ± 4.3 (5)
o-Xylene	139.1	-	8.4	1,095	88 ± 11 (12)	88 ± 3.0 (4)	84 ± 4.7 (6)
1,1,2,2-Tetrachloroethane	146.2	173	41	8,438	93 ± 4 (4)	88 ± 6 (7)	97 ± 7 (3)
m-Dichlorobenzene	173	948	20	3,606	103 ± 6 (4)	125 ± 5 (4)	131 ± 5 (4)
n-Decane	174.1	-	7.7	1,335	105 ± 32 (31)	111 ± 33 (30)	106 ± 20 (19)

(continued)

Table 24 (cont'd.)

Compound	B.P. (°C)	Breakthrough Volume (L)	ppb Sampled	Expected Quantity (ng/cartridge)	Storage Period		
					T_0 = 0 da	T_3 = 3 da	T_7 = 7 da
1,2,3-Trimethylbenzene	176.1	-	61.1	8,992	85 ± 14 (16)	79 ± 9.0 (11)	86 ± 5.8 (7)
Bis-(2-chloroethyl)ether	178	234	48	8,410	106 ± 5 (5)	85 ± 2 (2)	97 ± 3 (3)
o-Cresol	190.9	-	21.8	2,888	138 ± 20 (14)	89 ± 26 (29)	147 ± 22 (15)
Nitrobenzene	210.8	-	28.2	4,252	115 ± 22 (19)	108 ± 9.7 (90	117 ± 10 (8)
Benzyl chloride	215	830	12.1	1,868	146 ± 26 (18)	88 ± 29 (33)	165 ± 30 (18)

Table 25. PERCENT RECOVERY OF GROUP I COMPOUNDS FROM TENAX GC TRAPS - LOW LEVEL STUDY

Compound	Breakthrough Volume (L)	ppt Sampled	Expected Quantity (ng/cartridge)	Storage Period		
				T_0	T_5	T_7
Vinyl chloride	1	17	0.428	ND[a]	ND	ND
Methyl bromide	1	429	1.67	ND	ND	ND
Furan	3	542	4.55	ND	ND	ND
Acrylonitrile	5	858	9.43	ND	ND	ND
Chloroprene	15	2	0.85	ND	ND	ND
Chloroform	18	82	7.2	ND	ND	ND
Benzene	38	328	31.5	BI[b]	BI	BI
1,2-Dichloropropane	81	184	25.3	49.2 ± 8.9 (21)	37.7 ± 7	63.2 ± 39.8 (63)
Toluene	173	132	15.1	71.7 ± 9.3 (13)	53.3[c]	89.4
Tetrachloroethylene	380	161	32.8	BI	89.1	110.8
Chlorobenzene	344	95	13.1	43.2 ± 9.3 (22)	37.6 ± 24 (64)	77.6
1,1,2,2-Tetrachloroethane	173	351	72.6	BI	BI	BI
Bis-(2-chloroethyl)ether	234	252	43.8	BI	BI	BI
m-Dichlorobenzene	948	122	22.0	51.4 ± 6.4 (12)	22.0 ± 3.4 (16)	32.4 ± 4.7 (14)

higher than indicated here. There was no statistically significant trend indicating a decrease in recovery as a function of storage, nor was there a decrease in precision (Table 24). The reactivity of benzyl chloride and α-epichlorohydrin made it extremely difficult to calibrate, collect and analyze samples.

For chemicals with breakthrough volumes less than the sampling volume, the absolute recoveries were poor for many compounds as predicted (Table 26). After applying a correction for breakthrough, the recoveries were significantly better. For some chemicals, relative recoveries were still low. In all cases it is evident that the percent relative standard deviation for precision was considerably higher for these chemicals with low breakthrough volumes. Several reasons may apply. The first is that the absolute quantity accumulated on the Tenax® GC cartridges was small and coupled with high background of volatile organics, precise measurements were not possible with flame ionization detection. The use of a more specific detector, such as mass spectrometry (mass chromatography) reduces potential interferences. Secondly, these chemicals are easily influenced by displacement from more tenacious chemicals in the mixture sampled, an important factor to consider when using "chromatographic adsorbent traps". Finally, primary sources of standards for instrument calibration as certified standards are not available and thus uncertainty exists with accuracy of measurements.

It is interesting to note that even a compound (e.g. furan) with a breakthrough volume 1/10 of the sampling volume gave good recoveries based upon the breakthrough volume. Also, even at a total level of upto 600 ppb of vapors (for Group I compounds), premature breakthrough of furan, acrylonitrile, chloroprene, chloroform, benzene, etc. did not occur. Total levels higher than 600 ppb were not tested in this study. Thus, these data imply that only semi-quantitative determination for some vapor-phase organics can be at best expected for constituents with breakthrough volumes less than the sampling volume.

A chromatogram representing the analysis of a Tenax cartridge stored for seven days is depicted in Figure 33 (negative deflections are integrator event marks in all chromatograms).

Table 26. PERCENT RECOVERY OF TEST COMPOUNDS FROM TENAX GC TRAPS - DISREGARDING BREAKTHROUGH VOLUME (HIGH LEVEL STUDY)

Compound	Storage Period		
	T_0 = 0 da	T_3 = 3 da	T_7 = 7 da
Vinyl chloride	1.72 ± 0.98[a]	1.38 ± 0.22	1.67 ± 0.24
Methyl bromide	1.69 ± 0.24	2.11 ± 0.24	2.62 ± 0.08
Furan	7.89 ± 0.68	7.87 ± 1.99	7.85 ± 3.15
Acrylonitrile	20 ± 4.2	25 ± 3.37	29 ± 3.15
Chloroprene	19 ± 2.9	19 ± 0.15	21 ± 0.63
Chloroform	52 ± 9.8	65 ± 16	66 ± 13

[a] Percent ± S.D.

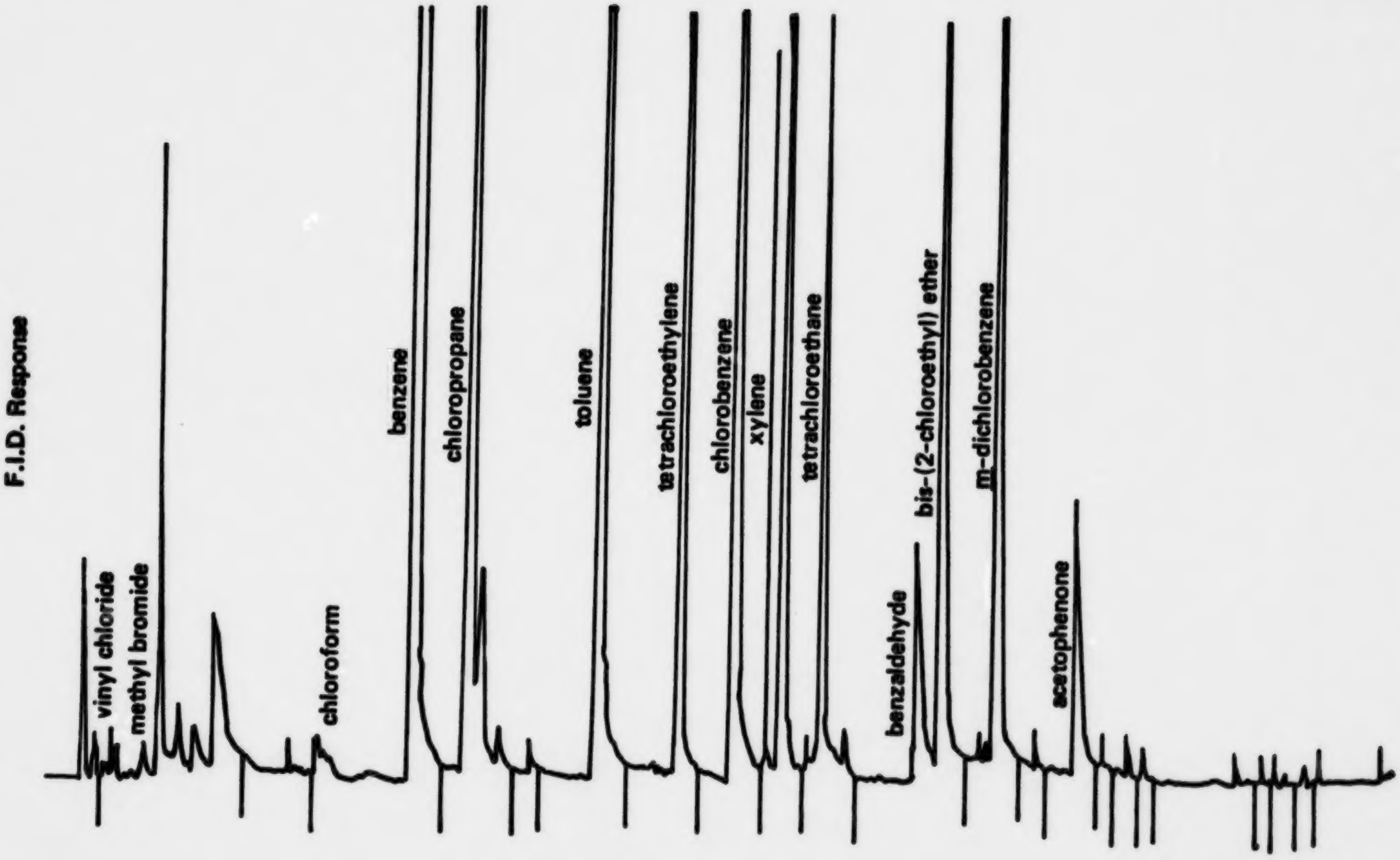

Figure 33. FID chromatogram of T_7 Tenax sample (high level study).

In contrast, only a few of the test compounds were detected in the low level study (Table 25) using TD/HRGC with flame ionization detection. The presence of background interferents was attributed to the air from the permeation/dilution system. Figure 34 presents the background observed for a typical Tenax® GC blank prior to its use in the sampling analysis studies at the low levels (electrometer sensitivity was set for low level nanogram detection). Figure 35 presents the background observed from the portable permeation system when sampling 30 L. Because of the low levels employed in this study and the use of an integrating collection device, background was experienced with the air from the permeation/dilution system. For these reasons, it was difficult to obtain precise and accurate determinations for several of the compounds. The recoveries observed after 7 days of storage for 1,2-dichloropropane, toluene, tetrachloroethylene, chlorobenzene were relatively better than for *m*-dichlorobenzene.

Charcoal Cartridges--The results of analysis of solvent desorbed charcoal tubes (High and Low Level Studies) by GC with electron capture detection are given in Table 27. The percent recovery for 1,2-dichloropropane and bis(2-chloroethyl)ether was considerably higher than for tetrachloroethylene and 1,1,2,2-tetrachloroethane. A decrease in recovery with storage time was observed. The lower recovery for the latter two compounds was probably due to the poor desorbing qualitities of the solvent mixture (carbon disulfide/-methanol:30/70). However, the use of a higher concentration of carbon disulfide which has been shown to be effective for desorbing substances from charcoal cannot be used with GC/ECD since the ECD exhibits a large response to this solvent. The percentage of carbon disulfide in methanol was selected to circumvent this problem.

A chromatogram for a sample stored three days prior to analysis is shown in Figure 36.

In the low level study no peaks were detected from charcoal traps (Table 27). The high background produced by the carbon disulfide/methanol obscured even the qualitative detection of tetrachloroethylene which was present at 33 pg/mL. An attempt was made to decrease the carbon disulfide concentration; however, the desorptive properties were then decreased to the extent that the problem of detection was aggravated.

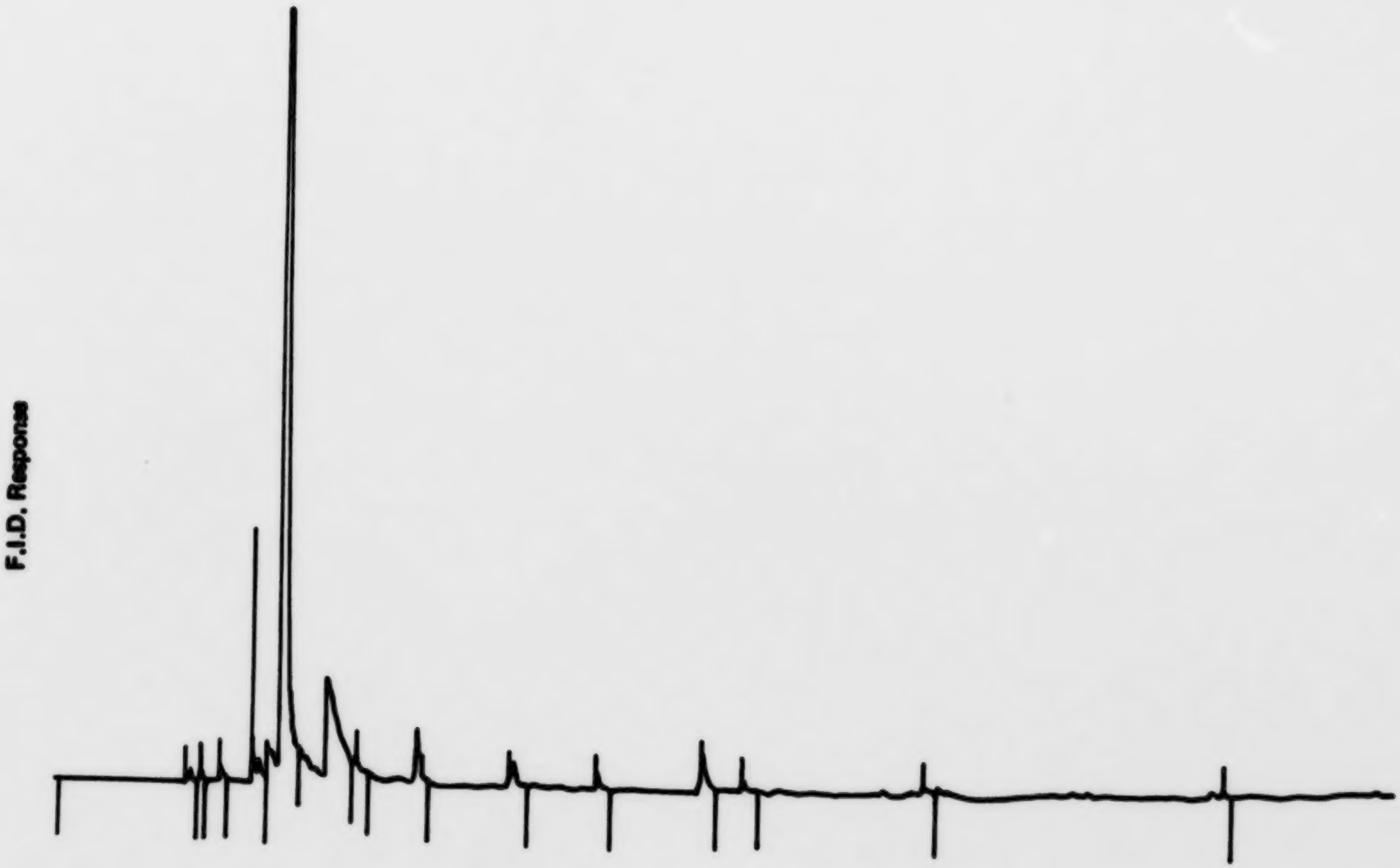

Figure 34. Background profile of Tenax® GC cartridge used in low level study.

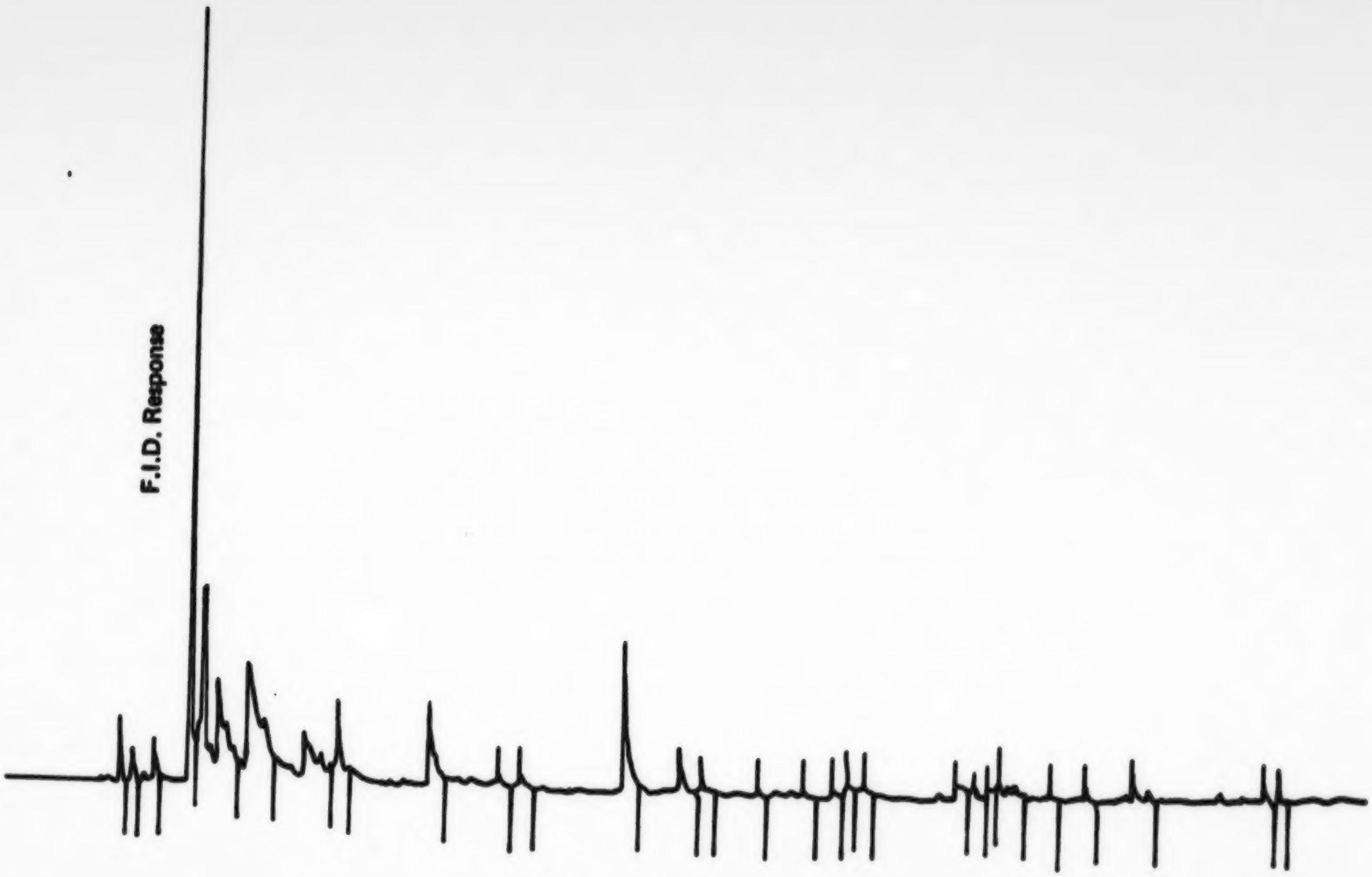

Figure 35. Background profile for 30 L of air from permeation/dilutor passed through a Tenax® GC cartridge.

Table 27. PERCENT RECOVERY OF GROUP I COMPOUNDS FROM CHARCOAL CARTRIDGES[a]

	High Level					Low Level				
			Storage Time					Storage Time		
Compound	ppb Sampled	Expected Quantity (ng/mL)	0 da	3 da	7 da	ppt Sampled	Expected Quantity (ng/mL)	0 da	3 da	7 da
Vinyl chloride	48	3,672	ND[b]	ND	ND	17	13	ND	ND	ND
Methyl bromide	80	5,587	ND	ND	ND	429	50	ND	ND	ND
Furan[c]	100	8,340	ND	ND	ND	542	46	ND	ND	ND
Acrylonitrile[c]	93	6,054	ND	ND	ND	858	57	ND	ND	ND
Chloroprene	4.5	487	ND	ND	ND	2	2	ND	ND	ND
Chloroform	15	2,196	ND	ND	ND	82	12	ND	ND	ND
Benzene[c]	60	5,742	ND	ND	ND	382	32	ND	ND	ND
1,2-Dichloropropane	24	3,326	90 ± 0.3 (0.33)[d]	88 ± 5.6 (6.4)	77 ± 5.5 (7.1)	184	25	ND	ND	ND
Toluene[c]	24	2,714	ND	ND	ND	132	15	ND	ND	ND
Tetrachloroethylene	30	6,102	34 ± 0.8 (2.3)	35 ± 2.0 (5.7)	35 ± 1.5 (4.2)	161	33	ND	ND	ND
Chlorobenzene	17	2,346	ND	ND	ND	95	13	ND	ND	ND
1,1,2,2-Tetrachloroethane	41	8,438	35 ± 1.6 (4.6)	32 ± 1.5 (4.7)	33 ± 1.0 (3.0)	351	73	ND	ND	ND
m-Dichlorobenzene	20	3,606	ND	ND	ND	122	22	ND	ND	ND
Bis-(2-chloroethyl)ether	48	8,410	86 ± 0.5 (0.6)	77 ± 4.3 (5.6)	66 ± 2.0 (3.0)	252	44	ND	ND	ND

[a] GC/ECD analysis.

[b] ND = not detected.

[c] Not sensitive in ECD.

[d] Mean ± S.D. (C.V.).

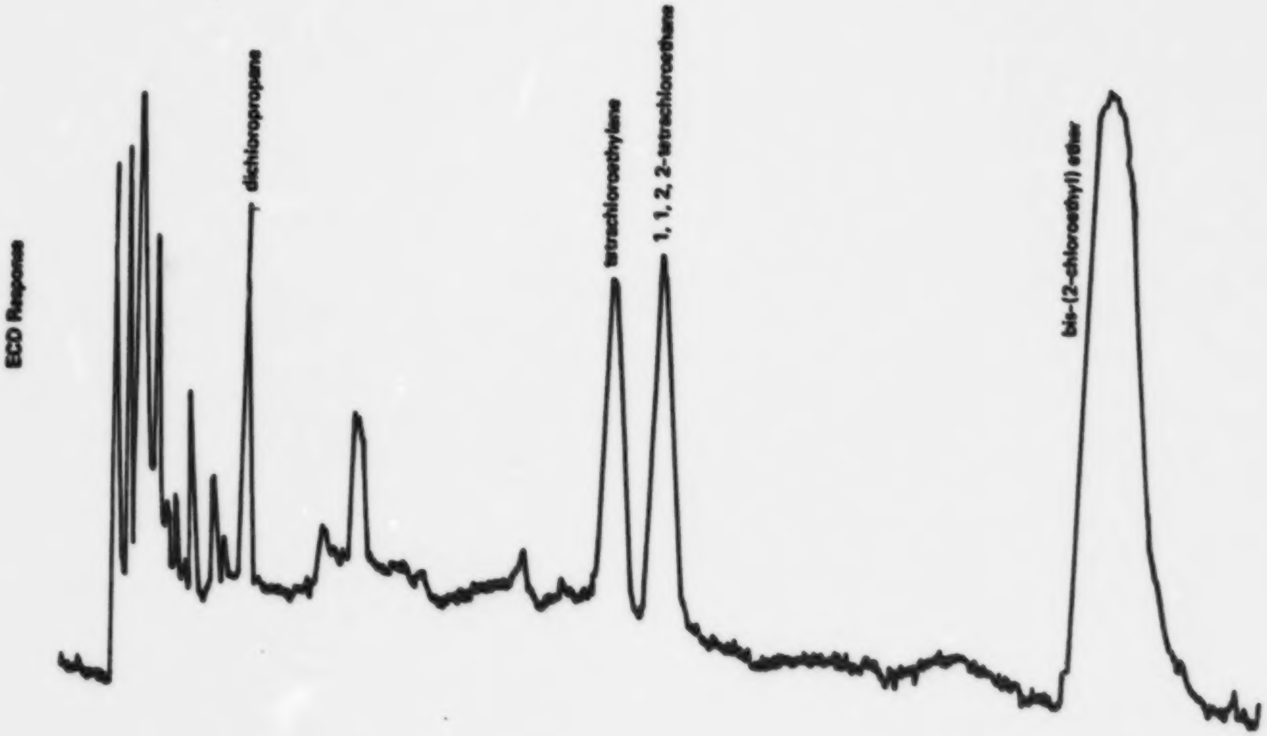

Figure 36. ECD chromatogram of T_3 carbon tube extract (high level study).

Cryogenic Traps--The percent recovery of Group I compounds from cryogenic traps is shown in Table 28 (High and Low Level Studies). In general the recoveries were extremely poor. This may be attributed to a low collection efficiency of unpacked nickel traps and/or utilizing dry ice as the cryogen in the high level study.

For the low level study the nickel cryogenic traps were packed with glass beads to increase the surface area prior to testing the collection efficiency. Concentrations of test substances down to 10 ppt were examined and again the results were poor for the very volatile organics and a large number of interfering substances inhibited successful low level detection of compounds (Table 28).

Interference Studies

Containers--

Interference studies were performed to determine the effects of O_3, NO_2, SO_2 and water vapor upon the recovery of the test compounds from the various containers. In the study, Group I and II compounds described earlier and "Summa" polished stainless steel containers, glass bulbs and Tedlar® bags were used.

By applying the appropriate calibration curve, the ppb level of each compound in each container was determined. The relative percent recovery was calculated from these measured ppb levels and the expected levels of each compound.

Anomalies--It has been seen in stability studies that the FID response to low concentrations of chloroprene and chloroform is small relative to most of the other compounds. In the interference studies, both the chloroprene and chloroform peaks were obscured by a large peak of unknown origin, preventing their quantitation. This interfering peak was present in the calibration analyses and analyses from all container types, but was not present in the control samples. This points to a permeation tube as a likely source for the contaminant. No data was reported for chloroprene or chloroform.

In our analytical scheme, furan and acrylonitrile peaks are generally not resolved and the data is reported as a sum of the two compounds. At the beginning of this calibration it was noted that the acrylonitrile

Table 28. PERCENT RECOVERY OF GROUP I COMPOUNDS FROM CRYOGENIC TRAPS - STORAGE/STABILITY STUDY

Compound	High Level			Low Level		
	0 da	3 da	7 da	0 da	3 da	7 da
Vinyl chloride	ND[a]	53	ND	ND	ND	ND
Methyl bromide	ND	ND	ND	ND	ND	ND
Furan	ND	94	ND	ND	ND	ND
Acrylonitrile	68 ± 3 (4)[b]	19	ND	ND	ND	ND
Chloroprene	4 ± 3 (75)	ND	ND	ND	ND	ND
Chloroform	39 ± 8 (21)	24 ± 6 (26)	20 ± 3 (16)	ND	ND	ND
Benzene	7 ± 5 (79)	ND	ND	102 ± 5.1 (5)	BI	BI
1,2-Dichloropropane	6 ± 5 (76)	14 ± 4 (29)	14 ± 3 (25)	ND	ND	ND
Toluene	1.6 ± 1.9 (113)	4 ± 1 (17)	3 ± 0.7 (27)	97.9 ± 1.7 (2)	I	I
Tetrachloroethylene	4 ± 3.5 (85)	1 ± 0.5 (50)	3 ± 0.02 (0.6)	72.5[c]	96.2 ± 39 (41)	I
Chlorobenzene	5 ± 6 (122)	8 ± 1.2 (15)	13 ± 11 (83)	I[d]	101.8	I
1,1,2,2-Tetrachloroethane	28 ± 37 (130)	61 ± 15 (25)	59 ± 7 (12)	I	I	I
Bis-(2-chloroethyl)ether	111 ± 13 (12)	77 ± 6 (21)	70 ± 12 (17)	I	I	I
m-Dichlorobenzene	27 ± 3 (10)	81 ± 13 (16)	61 ± 3 (5)	I	I	88.7

[a] ND = not detected.

[b] Mean ± S.D. (C.V.).

[c] Single value.

[d] I = Interference.

permeation tube had polymerized. For this reason the assumption was made that the contribution of acrylonitrile was very little in the calibration and container samples, and calculations for this peak were based on characteristics of furan only.

Tedlar® Bags--The recovery from the Tedlar® bags is presented in Table 29. Recovery is observed to be generally higher with low level interferences than with high level interferences. The interferences generally decreased the recoveries over those found in the storage study though some increases were observed. The fluctuations observed may be due to loss through chemical reaction, solubilization and/or displacement by water vapor on the container walls, and generation and/or release of other (organic) interferences.

Thus absolute recovery may have been higher for some compounds in the test mixtures than in the standard mixtures. The results of 1,2,3-trimethylbenzene are in question because the permeation rate doubled between weighings before and after the study. The recoveries of nitrobenzene are also questionable due to problems in calibration. Another trend seen was the large number of unknown peaks present in bags containing high level interferences as compared to bags with low level interferences. These interfering peaks prevented the quantification of bis-(2-chloroethyl)ether and m-dichlorobenzene. These interferences may have been released by the water vapor in the test sample.

No particular trends are noted in the precision of the recovery values. In fact, the precision values are similar for both high and low level interferences for most compounds.

Glass Bulbs--The recovery from the glass bulbs is presented in Table 30. The majority of the compounds showed higher recovery with the low-level interferences than with the high-level interferences. Recoveries were generally less than 100% for both high and low level interferences, though it is interesting to note that several compounds show substantially better recovery than in the storage study. The results of 1,2,3-trimethylbenzene and nitrobenzene are again questionable.

There appears again to be no particular trends with regard to precision.

Table 29. PERCENT RECOVERY OF TEST COMPOUNDS IN THE PRESENCE OF POTENTIAL INTERFERENCES FROM TEDLAR® BAGS

Compound	ppb Sampled	High Level	Low Level
Methyl chloride	55.8	65.7 ± 5.9 (8.9)	81.3 ± 2.3 (2.9)
Vinyl chloride	27.7	72.5 ± 4.3 (5.9)	92.6 ± 4.2 (4.6)
Methyl bromide	60.1	78.9 ± 2.7 (3.5)	85.4 ± 3.8 (4.4)
Methyl mercaptan	59.0	Not detected	Not detected
Furan/acrylonitrile[a]	39.6	38.6 ± 3.3 (8.6)	76.0 ± 12.7 (16.7)
Propylene oxide	27.3	Not detected	Not detected
Vinylidene chloride	20.9	37.5 ± 6.5 (17.4)	71.2 ± 4.9 (6.9)
Allyl chloride	87.5	57.7 ± 1.5 (2.6)	85.8 ± 2.2 (2.6)
Chloroprene[b]	2.1		
Chloroform[b]	8.1		
1,1,1-Trichloroethane	12.4	85.7 ± 3.7 (4.3)	81.5 ± 13.6 (16.7)
Benzene	32.4	67.8 ± 4.0 (5.9)	114.4 ± 15.3 (13.3)
1,2-Dichloropropane	17.5	109.3 ± 4.3 (4.0)	113.7 ± 9.6 (8.4)
Toluene	13.6	73.6 ± 4.6 (6.2)	87.5 ± 4.5 (5.2)
α-Epichlorohydrin	54.9	Not detected	Not detected
Tetrachloroethylene	12.4	109.7 ± 7.4 (6.7)	85.7 ± 3.5 (4.1)
Chlorobenzene	9.2	90.2 ± 2.9 (3.2)	88.3 ± 4.1 (4.6)
Ethylbenzene	7.4	72.0 ± 4.5 (6.3)	86.5 ± 1.4 (1.6)
o-Xylene	23.5	58.2 ± 1.2 (2.1)	68.5 ± 2.2 (3.2)
1,1,2,2-Tetrachloroethane	18.5	71.0 ± 3.6 (5.1)	72.5 ± 2.9 (4.0)
m-Dichlorobenzene	11.0	---[b]	62.5[c]

(continued)

Table 29 (cont'd.)

Compound	ppb Sampled	High Level	Low Level
n-Decane	6.5	63.5[c]	87.5[c]
1,2,3-Trimethylbenzene	66.0	42.3 ± 2.4 (5.8)	428.6 ± 22.7 (5.3)
Bis-(2-chloroethyl)ether	2.4	---[b]	62.5[c]
o-Cresol	20.9	Not detected	Not detected
Nitrobenzene	22.2	76.4 ± 0.3 (0.4)	84.4 ± 1.8 (2.1)
Benzyl chloride	28.6	69.6[d]	85.7[d]

[a] Based on furan only, acrylonitrile tube polymerized.

[b] Not quantified due to interfering peaks.

[c] Single observation.

[d] Only one measurement achieved due to interference.

Table 30. PERCENT RECOVERY OF TEST COMPOUNDS IN THE PRESENCE OF POTENTIAL INTERFERENCES FROM GLASS BULBS

Compound	ppb Sampled	High Level	Low Level
Methyl chloride	55.8	79.0 ± 1.2 (1.5)	75.4 ± 8.9 (11.8)
Vinyl chloride	27.7	94.2 ± 4.1 (4.3)	99.5 ± 0.5 (0.5)
Methyl bromide	60.1	82.3 ± 1.2 (1.4)	96.9 ± 2.2 (2.3)
Methyl mercaptan	59.0	Not detected	Not detected
Furan/acrylonitrile[a]	39.6	49.3 ± 2.6 (5.2)	78.6 ± 2.9 (3.7)
Propylene oxide	27.3	Not detected	Not detected
Vinylidene chloride	20.9	70.5 ± 24.3 (34.5)	66.1 ± 8.0 (12.1)
Allyl chloride	87.5	93.2 ± 3.1 (3.3)	85.3 ± 3.0 (3.5)
Chloroprene[b]	2.1		
Chloroform[b]	8.1		
1,1,1-Trichloroethane	12.4	101.0 ± 13.7 (13.5)	85.4 ± 4.9 (5.8)
Benzene	32.4	60.0 ± 3.4 (5.6)	90.3 ± 0.5 (0.5)
1,2-Dichloropropane	17.5	107.2 ± 2.0 (1.9)	96.0 ± 1.6 (1.6)
Toluene	13.6	80.6 ± 0.9 (1.1)	89.5 ± 2.3 (2.5)
α-Epichlorohydrin	54.9	Not detected	Not detected
Tetrachloroethylene	12.4	84.7 ± 14.6 (17.2)	93.8 ± 6.7 (7.1)
Chlorobenzene	9.2	89.9 ± 3.5 (3.9)	90.2 ± 5.4 (6.0)
Ethylbenzene	7.4	78.1 ± 4.2 (5.4)	88.2 ± 2.9 (3.3)
o-Xylene	23.5	62.6 ± 6.9 (11.0)	72.3 ± 1.4 (2.0)
1,1,2,2-Tetrachloroethane	18.5	83.8[c]	73.5 ± 1.6 (2.1)
m-Dichlorobenzene	11.0	92.4 ± 5.5 (5.9)	81.6 ± 9.1 (11.1)

(continued)

Table 30 (cont'd.)

Compound	ppb Sampled	High Level	Low Level
n-Decane	7.5	71.5 ± 6.6 (9.2)	82.9 ± 2.1 (2.6)
1,2,3-Trimethylbenzene	66.0	44.7 ± 8.7 (19.4)	539.3 ± 18.9 (3.4)
Bis-(2-chloroethyl)ether	2.4	83.3 ± 8.4 (10.0)	60.4 ± 4.2 (7.0)
o-Cresol	20.9	Not detected	Not detected
Nitrobenzene	22.2	75.9 ± 0.4 (0.6)	80.7 ± 4.2 (5.2)
Benzyl chloride	28.6	79.7 ± 7.8 (9.8)	87.5 ± 8.1 (9.3)

[a] Based on furan only, acrylonitrile tube polymerized.

[b] Not quantified due to interfering peaks.

[c] Single observation.

Summa Polished Steel Containers--The recovery from "Summa" polished steel containers is presented in Table 31. The level of interference appeared to have a significant effect upon the recovery of the majority of the compounds from "Summa" cans. The interferences generally decreased the recoveries over those found in the storage study, though, in fact, several recoveries were elevated by the presence of the interferences. Again fluctuations may be due to loss through chemical reaction, displacement by water vapor, and generation and/or release of other (organic) interferences.

As with the other containers, no general trends in precision are to be seen. It is noted however that very low recoveries and recoveries greater than 100% show exceptionally poor precision.

Traps--

The effects of inorganic pollutants on the recovery of test compounds using Tenax® GC, charcoal and cryogenic traps were investigated. Recovery of all compounds were evaluated only at the ppb level (Table 32) and were examined under several different experimental conditions (see Experimental Methods/Interference Study) which included sampling of test compounds (1) in the absence of inorganic pollutants, (2) in the presence of inorganic pollutants (with and without a glass fiber filter impregnated with ca. 5 mg of sodium thiosulfate prior to the Tenax® GC cartridge), and (3) at high and low levels of inorganic pollutants.

Tenax GC Cartridges--Table 32 presents the absolute recovery of test compounds for the control sample prior to the addition of inorganic pollutants. The levels of test substances ranged from 1 to 48 ppb. Because the breakthrough volumes were exceeded for the first six compounds listed and lower levels were employed than in the high level storage-stability studies several compounds were at trace levels or near background levels. The hydrocarbon background was traced to the NO supply.

Table 32 also list the absolute recovery of the test compounds in the presence of "high levels" of inorganic pollutants with and without a glass fiber filter preceding the Tenax® GC cartridge. These data indicate that the use of a glass fiber filter impregnated with sodium thiosulfate, a mild reducing agent, decreases the effect of inorganic gases on recovery of test compounds from Tenax® GC cartridges. Conversely, the percent recovery

Table 31. PERCENT RECOVERY OF TEST COMPOUNDS IN THE PRESENCE OF POTENTIAL INTERFERENCES FROM "SUMMA" POLISHED SS CANS

Compound	ppb Sampled	High Level	Low Level
Methyl chloride	55.8	71.9 ± 4.3 (6.0)	81.9 ± 1.8 (2.2)
Vinyl chloride	27.7	91.1 ± 6.5 (7.1)	98.5 ± 2.6 (2.6)
Methyl bromide	60.1	86.6 ± 3.0 (3.5)	95.4 ± 3.1 (3.2)
Methyl mercaptan	59.0	Not detected	Not detected
Furan/acrylonitrile[a]	39.6	54.7 ± 1.0 (1.9)	74.0 ± 6.3 (8.5)
Propylene oxide	27.3	Not detected	Not detected
Vinylidene chloride	20.9	56.4 ± 0.9 (1.5)	70.1 ± 6.7 (9.5)
Allyl chloride	87.5	79.6 ± 6.2 (7.8)	87.8 ± 1.2 (1.4)
Chloroprene[b]	2.1		
Chloroform[b]	8.1		
1,1,1-Trichloroethane	12.4	99.0 ± 4.6 (4.6)	82.0 ± 7.0 (8.6)
Benzene	32.4	73.6 ± 6.0 (8.1)	91.2 ± 1.5 (1.7)
1,2-Dichloropropane	17.5	111.3 ± 4.5 (4.0)	94.4 ± 2.9 (3.0)
Toluene	13.6	86.6 ± 2.8 (3.3)	88.3 ± 3.6 (4.1)
α-Epichlorohydrin	54.9	Not detected	Not detected
Tetrachloroethylene	12.4	118.6 ± 23.2 (20.0)	98.8 ± 3.4 (3.4)
Chlorobenzene	9.2	123.1 ± 17.7 (14.4)	84.5 ± 7.7 (9.1)
Ethylbenzene	7.4	64.2 ± 4.0 (6.2)	90.1 ± 0.5 (0.5)
o-Xylene	23.5	43.3 ± 5.5 (12.7)	73.0 ± 0.9 (1.3)
1,1,2,2-Tetrachloroethane	18.5	79.1 ± 7.9 (10.0)	74.9 ± 5.3 (7.1)
m-Dichlorobenzene	11.0	106.4 ± 5.2 (4.9)	76.6 ± 5.4 (7.0)

(continued)

Table 31 (cont'd.)

Compound	ppb Sampled	High Level	Low Level
n-Decane	7.5	62.0 ± 3.6 (5.8)	94.2 ± 13.1 (13.9)
1,2,3-Trimethylbenzene	66.0	23.7 ± 3.4 (14.3)	487.7 ± 18.9 (3.9)
Bis-(2-chloroethyl)ether	2.4	83.4 ± 5.9 (7.0)	60.4 ± 2.4 (4.0)
o-Cresol	20.9	Not detected	Not detected
Nitrobenzene	22.2	81.6 ± 0.9 (1.1)	88.9 ± 3.3 (3.7)
Benzyl chloride	28.6	76.9 ± 4.2 (5.4)	89.6 ± 4.8 (5.4)

[a] Based on furan only, acrylonitrile tube polymerized.

[b] Not quantified due to interfering peaks.

Table 32. ABSOLUTE RECOVERY OF GROUP I COMPOUNDS FROM TENAX® GC CARTRIDGES - HIGH LEVEL POTENTIAL INTERFERENCES

Compound	ppb Sampled	Expected Quantity (ng/cartridge)	(-) Inorganics[a]	(+) Inorganics[b]	
			No GFF	No GFF	GFF[c]
Vinyl chloride	17	165	T[d]	T	T
Methyl bromide	43	42	T	T	T
Furan	41	339	-	ND	ND
Acrylonitrile	48	520	-	-	-
Chloroprene	1	60	-	ND	ND
Chloroform	8	720	71 ± 25 (35)	54 ± 9 (17)	BI
Benzene	32	1,545	76 ± 5 (7)	40 ± 4 (10)	77 ± 8 (10)
1,2-Dichloropropane	19	2,580	63 ± 4 (6)	76 ± 5 (7)	92 ± 17 (18)
Toluene	14	1,530	78 ± 5 (6)	78 ± 3 (4)	82 ± 1 (1)
Tetrachloroethylene	16	3,440	78 ± 3 (4)	79 ± 4 (5)	75 ± 15 (20)
Chlorobenzene	10	1,350	77 ± 3 (4)	90 ± 5 (6)	84 ± 5[e]
1,1,2,2-Tetrachloroethane	24	4,864	118 ± 33 (28)	131 ± 30 (23)	118 ± 11 (9)
Bis-(2-chloroethyl)ether	25	4,350	69 ± 13 (19)	71 ± 16 (22)	69 ± 7 (10)
m-Dichlorobenzene	13	2,310	64 ± 6 (9)	77 ± 11 (14)	67 ± 0.2 (0.3)

[a] Synthetic air/vapor mixture sampled, no O_3, NO_2, SO_2 or humidity was present.

[b] Synthetic air/vapor mixture sampled, potential interferences present.

[c] GFF = glass fiber filter impregnated with sodium thiosulfate (ca. 5 mg) was used prior to the cartridge.

[d] T = trace, - = weak signal not resolved from background, ND = not detected, BI = background interference.

[e] Duplicate analysis only.

increased for benzene and 1,2-dichloropropane. A possible explanation is that ozone is quenched by the reducing agent prior to reaching the adsorbent and thus the adsorbed test compounds are not destroyed. In the case of furan and chloroprene, these compounds may have reacted (depleted) with the high levels of ozone while in transit through the permeation/dilution system prior to reaching the sampling device.

Table 33 gives the relative percent recoveries for all compounds tested. Relative percent recoveries were calculated as a ratio of absolute recovery observed in the presence of inorganic pollutants to the absolute recovery observed in the absence of inorganic pollutants times 100 percent. These data suggest a trend since inorganic pollutants lower the recovery of furan, chloroprene, chloroform, and benzene (see Tables 32 and 33/no GFF).

Table 33 also gives the relative percent recoveries for sampling and analysis of test compounds in the presence of "low levels" of inorganic pollutants. These data indicate that lower levels of inorganic pollutants did not completely react with furan, chloroprene, and acrylonitrile during their transit time in the permeation/dilution system. Since sufficient test substance reached the Tenax® GC cartridge differences between sampling with and without a GFF were demonstratable for these compounds. Except for α-epichlorohydrin the recoveries for other test substances were similarly unaffected by "lower levels" of inorganic pollutants i.e. their recoveries were already as high as the "control" experiment.

Table 34 gives the relative percent recovery for Group II compounds observed without correction for breakthrough volume. Thus, comparison of Tables 33 and 34 reveals the differences when taking the breakthrough volume into account relative to the sampling volume.

Figures 37 through 40 depict a few example chromatograms for various experimental conditions.

Charcoal Cartridges--Tables 35 and 36 present the percent recoveries of test compounds from charcoal cartridges in the presence of high and low levels of inorganic gases. Because of a contaminant from charcoal (see Section 7 for identification), it was not possible to quantify bis(2-chloroethyl)ether. Thus, only results for 1,1,2,2-tetrachloroethane and tetrachloroethylene were obtained. The data (Tables 35 and 36) includes absolute

Table 33. RELATIVE PERCENT RECOVERY OF TEST COMPOUNDS FROM TENAX® GC CARTRIDGES - INTERFERENCE STUDY WITH CORRECTION FOR BREAKTHROUGH VOLUME

Compound	B.P. (°C)	Breakthrough Volume (ℓ)	ppb Sampled	High Level[a] No GFF	High Level[a] GFF[b]	Low Level No GFF	Low Level GFF
Methyl chloride	-24.2	3	55.8	3.[illegible] ± 2.1 (60)	10 ± 1.7 (17)	2.9 ± 2.6 (91)	4.6 ± 1.3 (28)
Vinyl chloride	-13	1	17	T[c]	T	T	T
Methyl bromide	3.4	1	43	T	T	T	T
Methyl mercaptan	6.2	-	59	ND	ND	ND	ND
Furan	31.4	3	41	NC	ND	42 ± 7 (17)	111 ± 21 (19)
Propylene oxide	34.3	4	27.3	T	19 ± 8.9 (5)	18 ± 11 (65)	37 ± 4.7 (13)
Acrylonitrile		5	48	NC	NC	I	I
Vinylidene chloride	37	1	20.9	50 ± 21 (42)	239 ± 131 (55)	39 ± 27 (70)	127 ± 34 (27)
Allyl chloride	45	6	87.5	4.9 ± 1.2 (24)	18 ± 3.4 (18)	7.4 ± 4.0 (54)	30 ± 2.1 (7.2)
Chloroprene	59.4	15	1	ND	ND	48 ± 13 (27)	112 ± 39 (35)
Chloroform	61.7	18	8	76 ± 36 (47)	NC	100 ± 44 (44)	I
1,1,1-Trichloroethane	74.1	9	12.4	6.7 ± 1.2 (18)	101 ± 10 (10)	8.0 ± 3.6 (45)	77 ± 10 (13)
Benzene	77	38	32	53 ± 9 (17)	101 ± 8 (8)	47 ± 10 (11)	100 ± 10 (10)
1,2-Dichloropropane	96.4	81	19	120 ± 11 (9)	146 ± 19 (12)	82 ± 7 (9)	129 ± 12 (9)
Toluene	110.6	173	14	100 ± 7 (7)	105 ± 6 (6)	97 ± 3 (3)	103 ± 5 (5)
α-Epichlorohydrin	116.5	54	54.9	39 ± 6.1 (15)	104 ± 14 (13)	34 ± 15 (44)	92 ± 12 (13)
Tetrachloroethylene	121	380	16	101 ± 7 (7)	96 ± 11 (11)	94 ± 6 (6)	111 ± 7 (6)
Chlorobenzene	132	344	10	116 ± 8 (7)	109 ± 9 (8)	96 ± 2 (2)	106 ± 2 (2)
Ethylbenzene	136.2	344	7.4	40 ± 1 (2.5)	63 ± 11 (17)	43 ± 18 (42)	75 ± 7.5 (10)
o-Xylene	139.1	-	23.5	51 ± 2.2 (4.4)	85 ± 15 (18)	55 ± 23 (42)	96 ± 11 (11)
1,1,2,2-Tetrachloroethane	146.2	173	24	111 ± 40 (36)	100 ± 30 (30)	80 ± 22 (28)	126 ± 50 (40)
m-Dichlorobenzene	173	948	13	120 ± 17 (14)	104 ± 6 (5.7)	83 ± 6 (7)	91 ± 11 (12)

(continued)

Table 33 (cont'd.)

Compound	B.P. (°C)	Breakthrough Volume (ℓ)	ppb Sampled	High Level No GFF	High Level GFF	Low Level No GFF	Low Level GFF
n-Decane	174.1	-	7.5	24 ± 4.0 (8.4)	38 ± 6.4 (17)	I	I
1,2,3-Trimethylbenzene[d]	176.1	-	66	13 ± 0.3 (2.2)	24 ± 4.0 (16)	I	I
Bis-(2-chloroethyl)ether	178	234	25	103 ± 31 (30)	100 ± 20 (20)	98 ± 21 (21)	111 ± 38 (34)
o-Cresol	190.9	-	20.9	I	I	I	I
Nitrobenzene	210.8	-	22.2	79 ± 0.7 (0.9)	139 ± 19 (14)	112 ± 47 (42)	93 ± 35 (38)
Benzyl chloride	215	830	28.6	24 ± 2.3 (9.7)	58 ± 7.9 (14)	I	I

[a] See Table 10 for levels of inorganic gases employed.

[b] GFF = glass fiber filter impregnated with sodium thiosulfate.

[c] T = trace, ND = not detected, NC = not calculated, I = interference, values are mean ± S.D. (C.V.) for triplicate samples.

[d] Permeation tube was highly suspect.

Table 34. RELATIVE PERCENT RECOVERY OF GROUP II COMPOUNDS FROM TENAX® GC CARTRIDGES - INTERFERENCE STUDY, UNCORRECTED FOR BREAKTHROUGH VOLUME

Compound	Breakthrough Vol. (L) @ 90°F	ppb Sampled	High Level		Low Level	
			No. GFF	GFF	No GFF	GFF
Methyl mercaptan	-	59.0	2.5 ± 1.0 (42)	8.3 ± 8.0 (98)	4.6 ± 2.3 (51)	9.6 ± 2.5 (25)
Vinylidene chloride	1.0	20.9	1.7 ± 0.7 (42)	9.6 ± 5.3 (55)	1.3 ± 0.9 (70)	5.1 ± 1.4 (27)
Methyl chloride	3	55.8	0.4 ± 0.2 (50)	1.4 ± 0.2 (17)	0.3 ± 0.3 (100)	0.6 ± 0.2 (30)
Propylene oxide	4	27.3	T[a]	3.2 ± 1.5 (47)	2.3 ± 1.5 (65)	6.2 ± 0.8 (13)
Allyl chloride	6	87.5	1.0 ± 0.2 (23)	5.5 ± 1.0 (19)	1.5 ± 0.8 (54)	8.9 ± 0.6 (7)
1,1,1-Trichloroethane	9	12.4	5.4 ± 1.0 (18)	40 ± 4.1 (10)	6.5 ± 2.9 (45)	31 ± 4.2 (14)
α-Epichlorohydrin	54	54.9	39 ± 6.1 (15)	104 ± 14 (13)	34 ± 15 (44)	92 ± 12 (13)
n-Decane	>30	7.5	24 ± 2.0 (8)	38 ± 6.4 (17)	I	I
o-Cresol	>30	20.9	I[b]	I	I	I
o-Xylene	>30	23.5	51 ± 2.2 (4)	85 ± 15 (18)	55 ± 23 (42)	96 ± 11 (11)
Ethylbenzene	344	7.4	40 ± 1 (2)	63 ± 11 (18)	43 ± 18 (42)	75 ± 7.5 (10)
1,2,3-Trimethylbenzene	>30	66.0	13 ± 0.3 (2)	24 ± 4.0 (16)	I	I
Benzylchloride	830	28.6	24 ± 2.3 (10)	58 ± 8.0 (14)	I	I
Nitrobenzene	>30	22.2	79 ± 0.7 (0.9)	139 ± 19 (14)	112 ± 47 (43)	93 ± 35 (38)

[a] T = trace.

[b] I = interference.

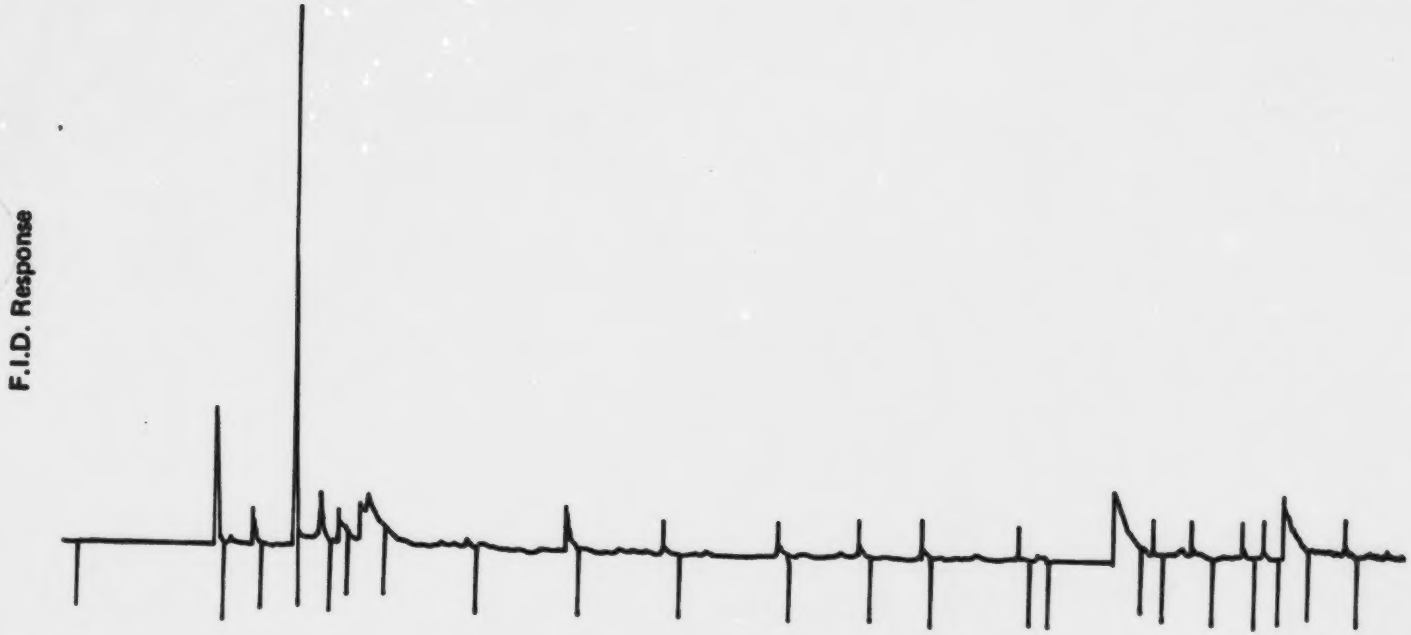

Figure 37. Chromatogram for background observed with Tenax used to sample 30 L of air containing low levels of inorganic gases (no GFF).

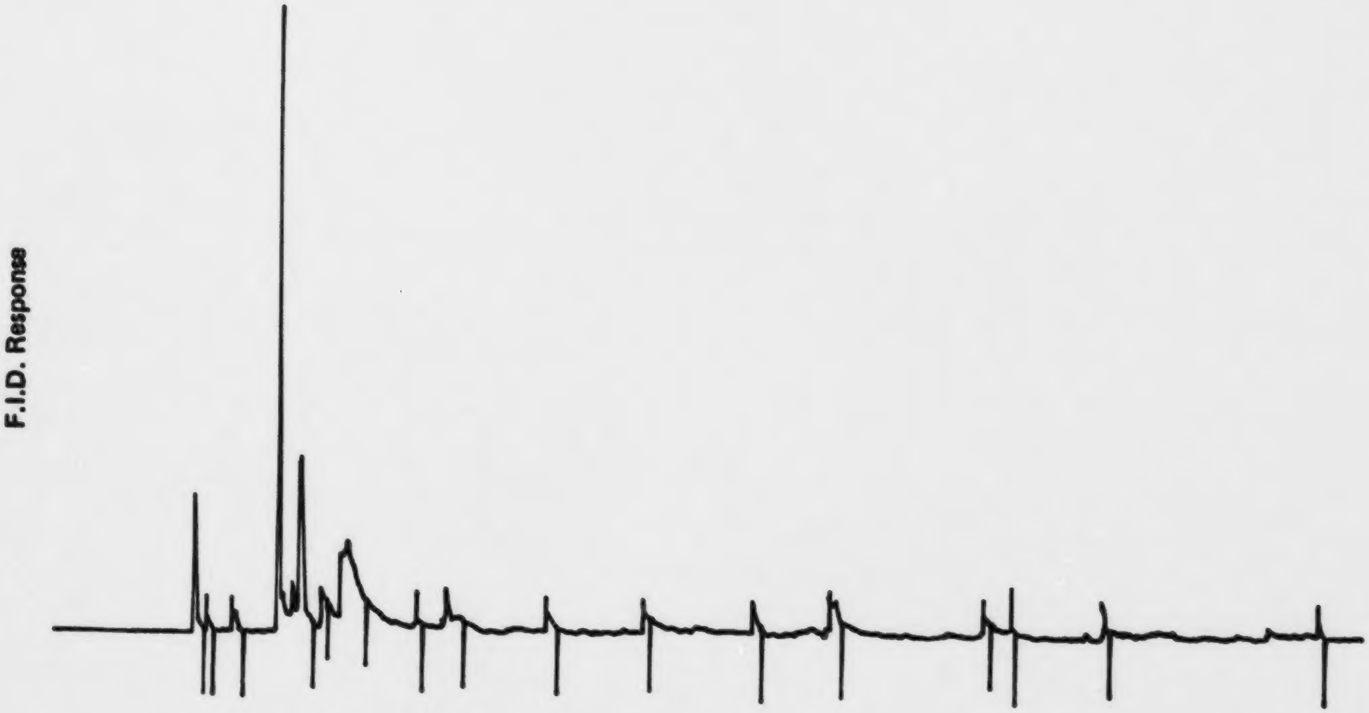

Figure 38. Chromatogram of background observed with Tenax used to sample 30 L air containing low levels of inorganic gases (with GFF).

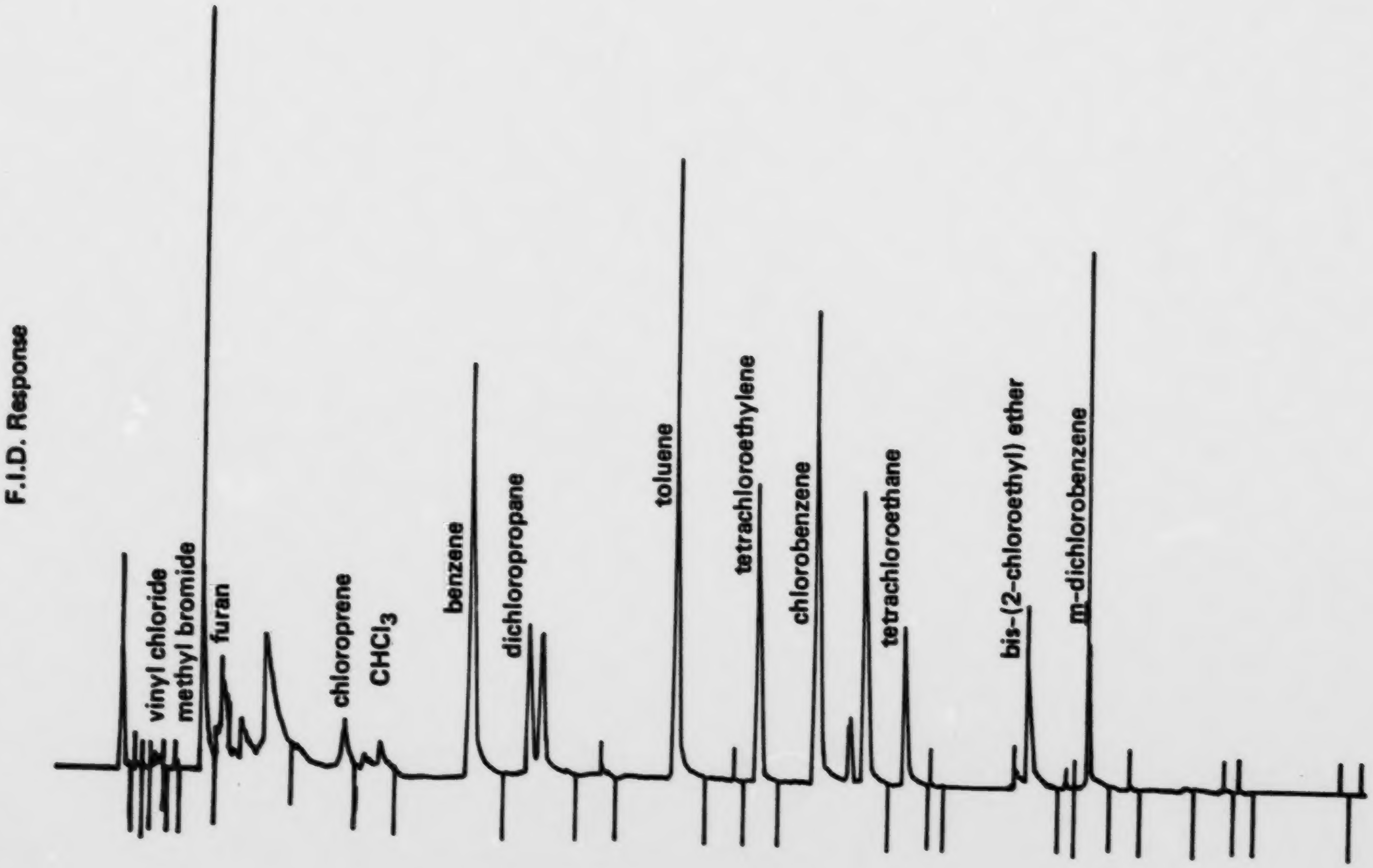

Figure 39. Chromatogram for sample taken with Tenax with test compounds and low levels of inorganic gases present (no GFF).

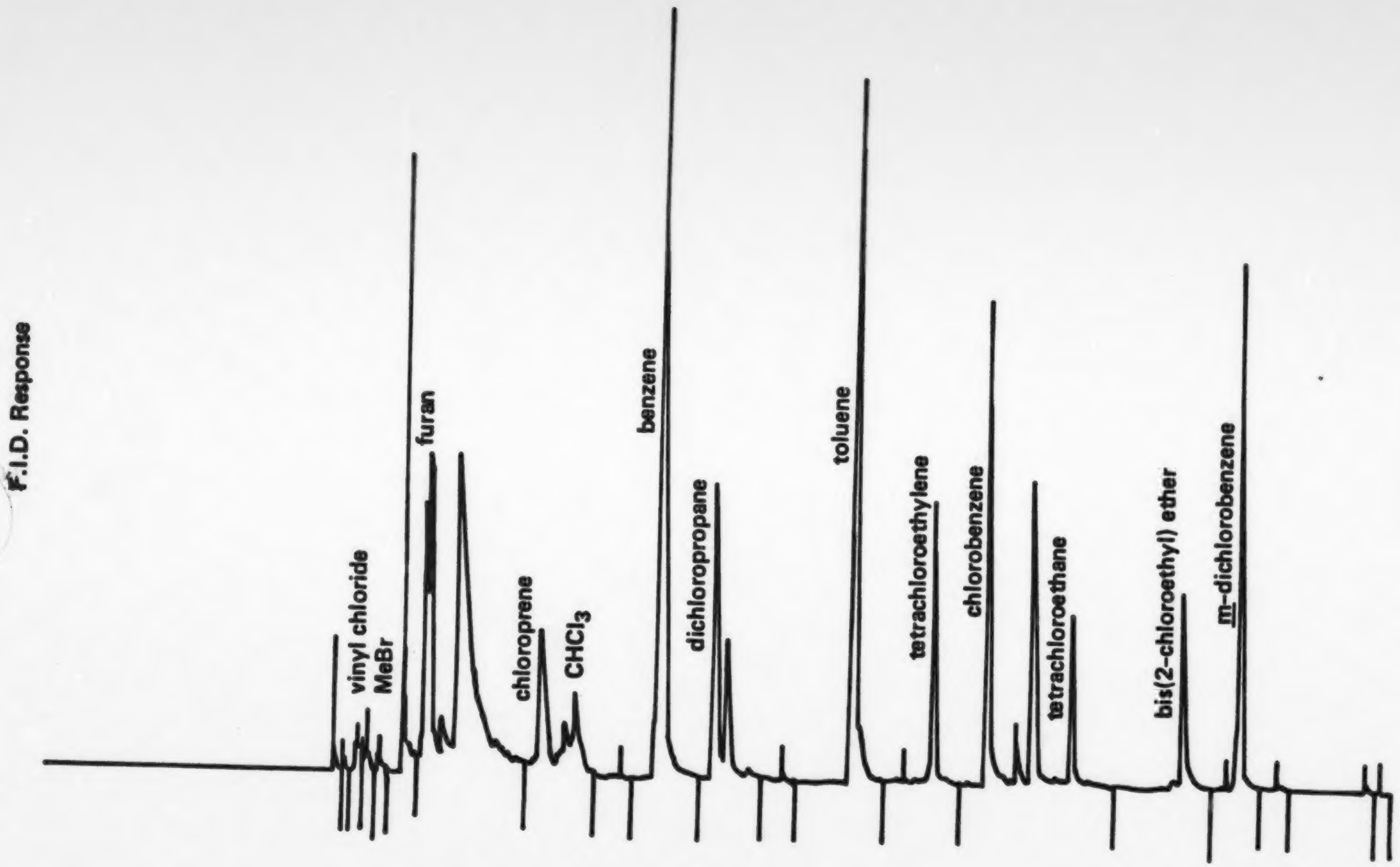

Figure 40. Chromatogram for sample taken with Tenax with test compounds and low levels of inorganic gases present (with GFF).

Table 35. PERCENT RECOVERIES OF GROUP I COMPOUNDS FROM CHARCOAL CARTRIDGES IN THE PRESENCE OF HIGH LEVELS OF INORGANIC SUBSTANCES[a]

Compound	Percent Recovery ± S.D. (C.V.)		
	Absolute/-I.S.[b]	Absolute/+ I.S.	Relative[c]/+ I.S.
m-Dichlorobenzene	-[d]	-	-
Bis-(2-Chloroethyl)ether	BI[e]	BI	BI
1,1,2,2-Tetrachloroethane	ND	43 ± 11 (26)	ND
Chlorobenzene	-	-	-
Tetrachloroethylene	54 ± 12 (22)	80 ± 42 (52)	148 ± 84 (57)
Toluene	-	-	-
1,2-Dichloropropane	-	-	-
Benzene	-	-	-
Chloroform	-	-	-
Chloroprene	-	-	-
Acrylonitrile	-	-	-
Furan	-	-	-
Methyl bromide	-	-	-
Vinyl chloride	-	-	-

[a] See Table 10 for concentrations of inorganic substances.

[b] IS = inorganic substances absent (-) or present (+).

[c] Recoveries are relative to "control" which was collection in the absence of inorganic substances.

[d] Compounds not detected by this analysis procedure.

[e] ND = not detected, BI = background interference.

Table 36. PERCENT RECOVERIES OF GROUP I COMPOUNDS FROM CHARCOAL CARTRIDGES IN THE PRESENCE OF LOW LEVELS OF INORGANIC SUBSTANCES[a]

Compound	Percent Recovery ± S.D. (C.V.)		
	Absolute/-I.S.[b]	Absolute/+ I.S.	Relative[c]/+ I.S.
m-Dichlorobenzene	-[d]	-	-
Bis-(2-Chloroethyl)ether	BI[e]	BI	BI
1,1,2,2-Tetrachloroethane	ND	T[e]	ND
Chlorobenzene	-	-	-
Tetrachloroethylene	117 ± 7 (6)	60 ± 31 (52)	51 ± 27 (52)
Toluene	-	-	-
1,2-Dichloropropane	-	-	-
Benzene	-	-	-
Chloroform	-	-	-
Chloroprene	-	-	-
Acrylonitrile	-	-	-
Furan	-	-	-
Methyl bromide	-	-	-
Vinyl chloride	-	-	-

[a] See Table 10 for concentrations of inorganic substances.

[b] IS = inorganic substances absent (-) or present (+).

[c] Recoveries are relative to "control" which was collection in the absence of inorganic substances.

[d] Compounds not detected by this analysis procedure.

[e] ND = not detected, BI = background interference.

recoveries in the absence and presence of inorganic gases and the relative recoveries between the two. This phenomenon was also observed but to a smaller degree with low levels of inorganic gases. A possible explanation may be that charcoal tubes prior to sampling are highly activated and while sampling is conducted in the presence of humidity, the charcoal sorbent becomes deactivated and thus the adsorbed analytes are more easily desorbed with organic solvent than when the analytes are adsorbed to an activated charcoal surface.

The other analytes in Tables 35 and 36 are listed only for reference purpose. Electron capture detection does not detect these compounds because of their poor electron affinity. Figures 41 through 46 present typical chromatograms obtained during the interference studies.

The results utilizing charcoal in both the storage-stability study and in the pollutant interference study were somewhat disappointing since the number of compounds which could actually be detected (FID and ECD) using this sorbent were rather few.

Cryogenic Traps--Since sampling and analysis with Ni cryogenic traps packed with glass beads using dry ice was not fruitful in the storage-stability studies, liquid oxygen was used as the coolant in these experiments.

Tables 37 and 38 present the absolute percent recovery of test compounds from cryogenic traps in the presence of high and low levels of inorganic gases. Once again inconsistent background of the cryogenic trap yielded large coefficients of variation. Given in each Table are the results for the presence and absence of the standard inorganic pollutants. Differences in recovery were observed between the two experimental conditions. The recovery of vinyl chloride, methyl bromide, furan, chloroprene, chloroform, and benzene all decreased when inorganic gases were present during sampling. The coefficient of variations for triplicate analysis were large for other compounds. The absolute recoveries appeared to be less than those observed with Tenax® GC traps.

Another problem arises with the cryogenic traps when using liquid oxygen. Excessive amounts of water were trapped and subsequently transferred to the Tenax cartridge during the purging step. In order to analyze by TD/HRGC, the large quantities of water were removed by placing calcium

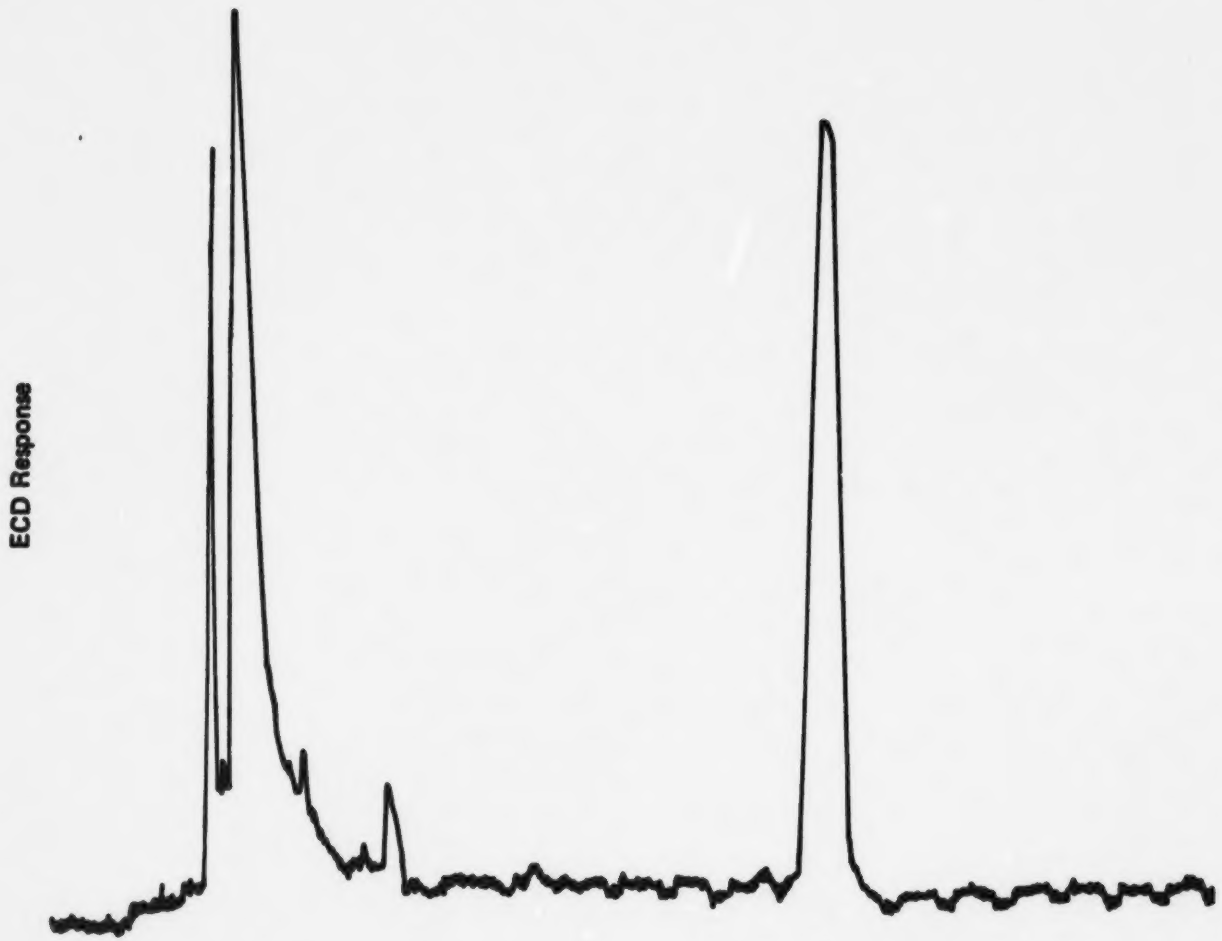

Figure 41. Chromatogram of background for 30 L air sample taken with charcoal trap in the presence of high levels of inorganics and no test model compounds.

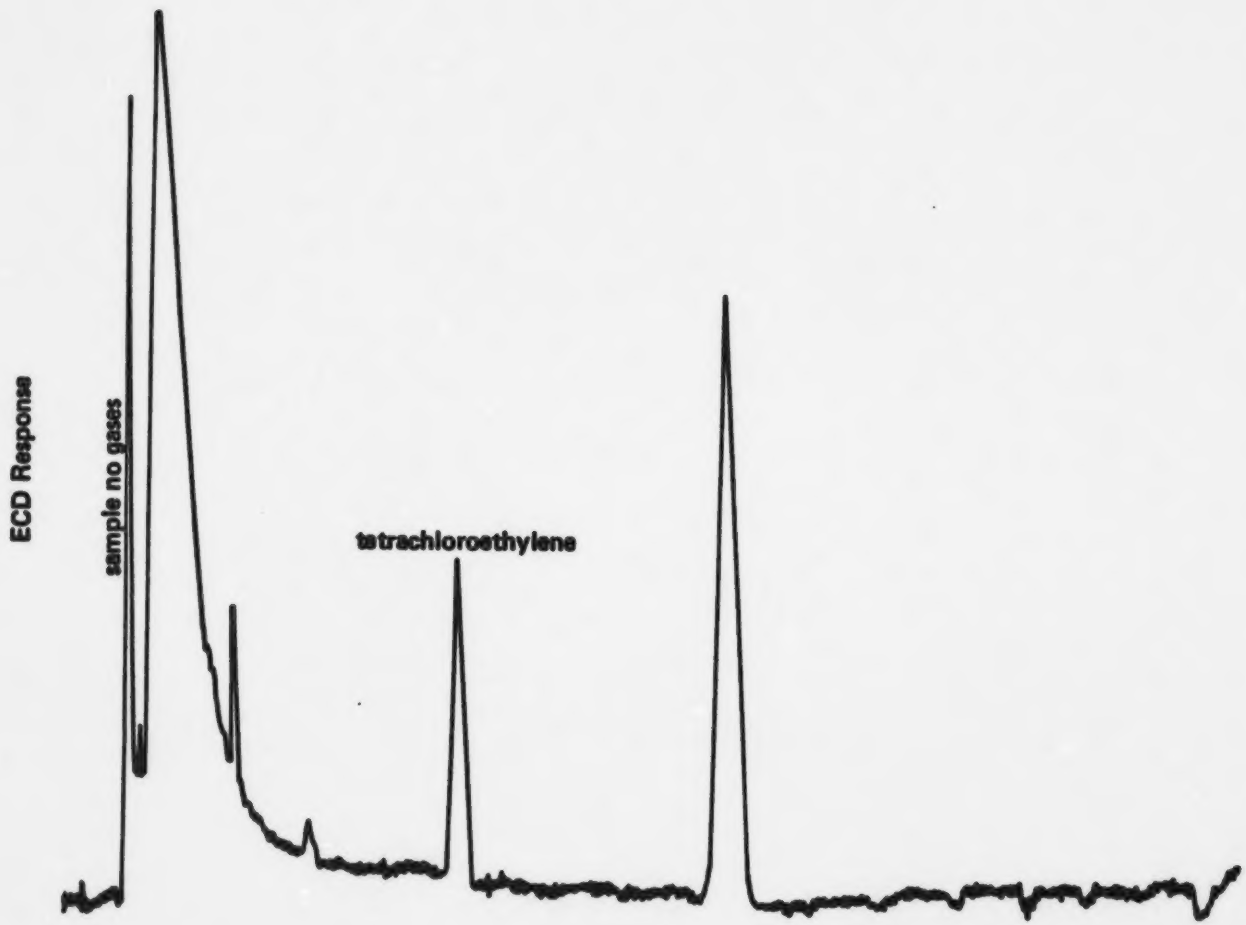

Figure 42. Chromatogram for 30 L air sample in the absence of inorganics (high level study) and with test model compounds.

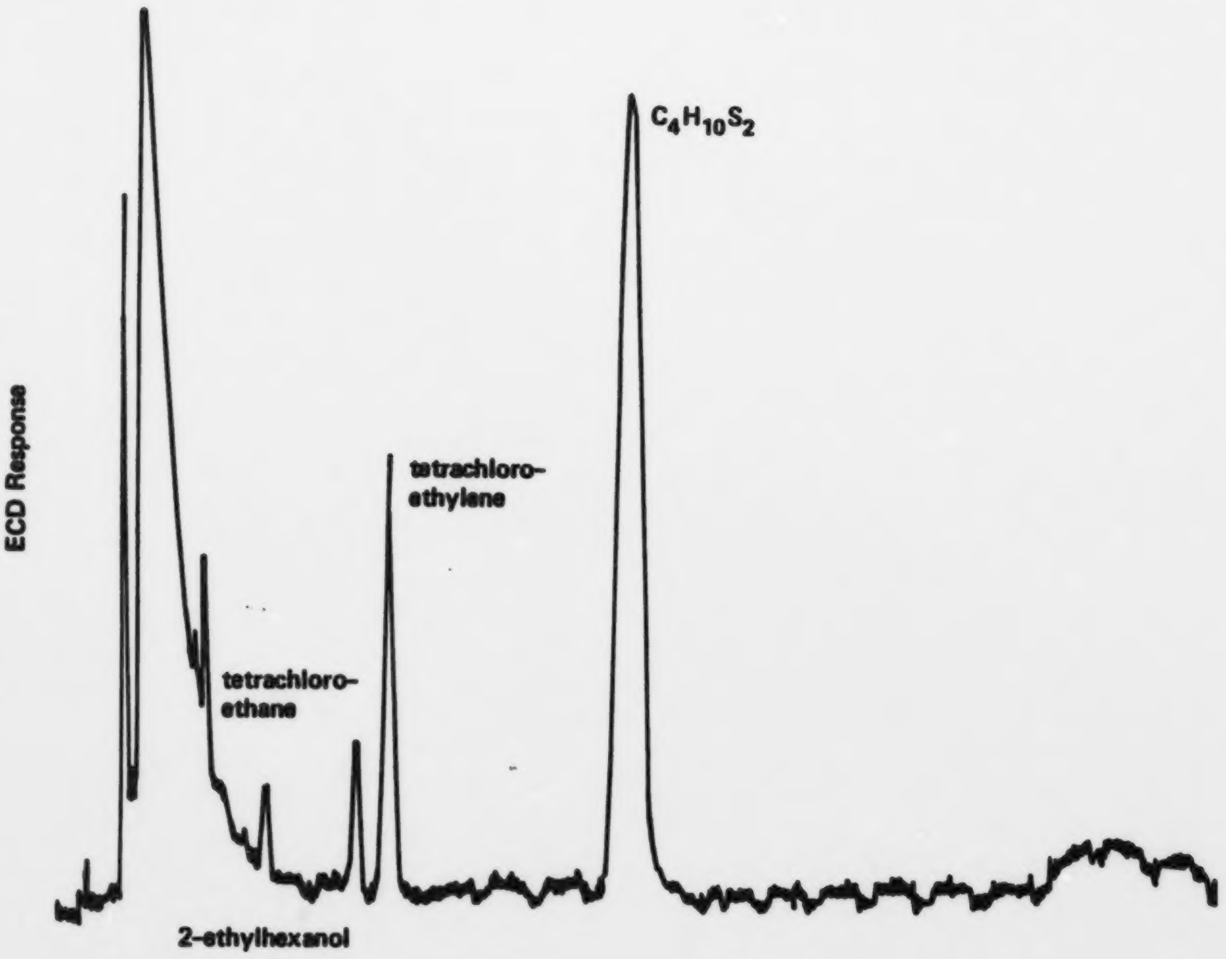

Figure 43. Chromatogram of 30 L air sample with charcoal trap in the presence of high levels of inorganics and test model compounds.

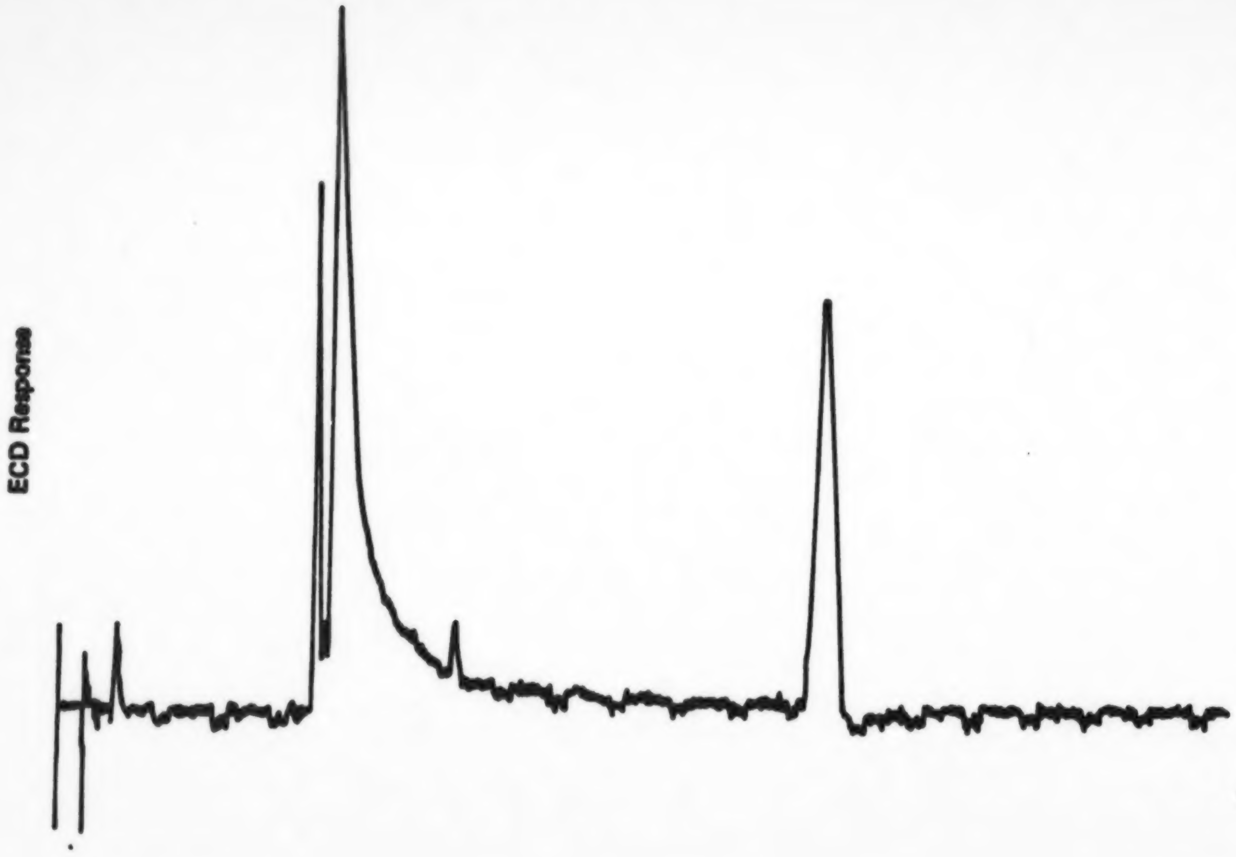

Figure 44. Chromatogram of background for 30 L air sample taken with charcoal trap in the presence of low levels of inorganics and no test compounds.

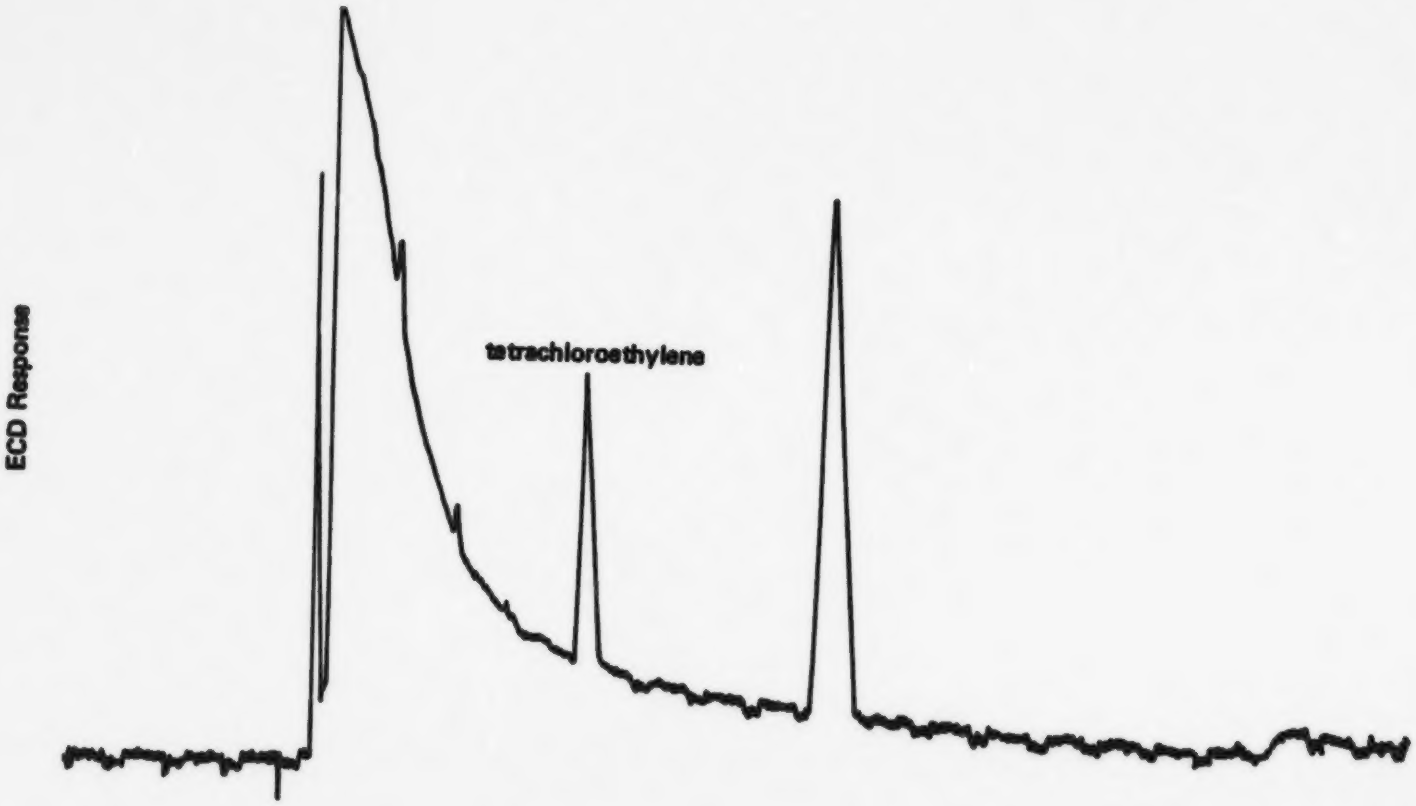

Figure 45. Chromatogram for 30 L air sample with charcoal trap in the absence of inorganics (low level study) and test compounds present.

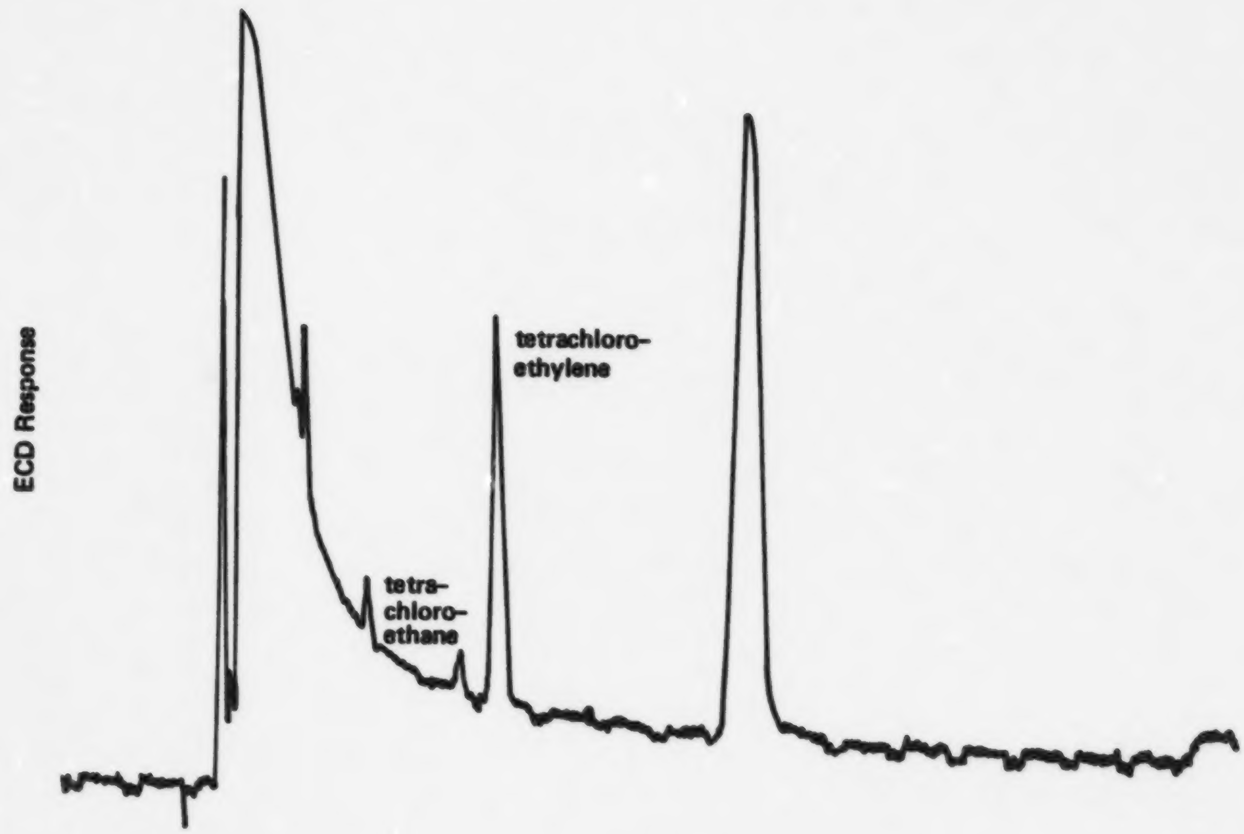

Figure 46. Chromatogram of 30 L air sample using charcoal trap and low levels of inorganics and test compounds present.

Table 37. ABSOLUTE PERCENT RECOVERY OF GROUP I COMPOUNDS FROM CRYOGENIC TRAPS IN THE PRESENCE OF HIGH LEVELS OF INORGANIC SUBSTANCES[a]

Compound	(-) Standard Pollutants	(+) Standard Pollutants
m-Dichlorobenzene	15 ± 3 (20)	28 ± 1 (4)
Bis-(2-chloroethyl)ether	20 ± 5 (25)	28 ± 5 (18)
1,1,2,2-Tetrachloroethane	55 ± 11 (20)	65 ± 9 (14)
Chlorobenzene	35 ± 8 (23)	32 ± 7 (22)
Tetrachloroethylene	30 ± 11 (37)	28 ± 10 (36)
Toluene	42 ± 13 (31)	26 ± 9 (35)
1,2-Dichloropropane	22 ± 6 (27)	25 ± 21 (84)
Benzene	41 ± 14 (34)	21 ± 19 (90)
Chloroform	93 ± 28 (30)	20 ± 7 (35)
Chloroprene	18 ± 7 (39)	ND
Acrylonitrile	BI	BI
Furan	T	ND
Methyl bromide	T	T
Vinyl chloride	T	T

[a] See Table 10 for concentrations of inorganic substances employed. Recoveries are based upon the calculated amounts in the synthetic air/vapor stream sampled. Mean ± S.D. (C.V.) are for triplicate samples.

[b] BI = background interference, ND = not detected, T = trace.

Table 38. ABSOLUTE PERCENT RECOVERY OF GROUP I COMPOUNDS USING CRYOGENIC TRAPS - LOW LEVEL POTENTIAL INTERFERENCES

Compound	ppb Sampled	(-) Inorganics[a]	(+) Inorganics
Vinyl chloride	17	23 ± 8 (35)	22 ± 28 (127)
Methyl bromide	43	53 ± 25 (47)	27 ± 28 (104)
Furan	41	50 ± 1 (2)	ND[b]
Acrylonitrile	48	BI	BI
Chloroprene	1	32 ± 7 (22)	22 ± 16 (73)
Chloroform	8	126 ± 26 (21)	66 ± 33 (50)
Benzene	32	50 ± 22 (44)	26 ± 18 (69)
1,2-Dichloropropane	19	72 ± 5 (7)	30 ± 16 (53)
Toluene	14	54 ± 3 (6)	31 ± 16 (52)
Tetrachloroethylene	16	61 ± 5 (8)	31 ± 18 (58)
Chlorobenzene	10	66 ± 6 (9)	34 ± 11 (32)
1,1,2,2-Tetrachloroethane	24	107 ± 47 (44)	42 ± 18 (43)
Bis-(2-chloroethyl)ether	25	33 ± 9 (27)	18 ± 6 (33)
_m_-Dichlorobenzene	13	58 ± 10 (17)	30 ± 7 (23)

[a] Synthetic air/vapor mixture sampled without and with inorganic gases present.

[b] ND = not detected, BI = background interference, values are mean ± S.D. (C.V.) of triplicate samples.

sulfate in the bottom of the culture tube to adsorb moisture from the glass wool used to secure the Tenax® GC in the cartridge. This procedure solved the problem of excess water. Other studies have shown that this drying step is quantitative (20).

Table 39 presents the relative percent recovery of test compounds from cryogenic traps in the presence of high levels of inorganic substances. These data were calculated as recoveries relative to the control which was the collection of test compounds in the absence of inorganic gases. Even though a large coefficient of variation was observed, considerable differences between the control (no standard pollutant) and experimental sample are evident. Inconsistent trapping of organic test vapors and background from the cryogenic traps contributed to the observed large coefficient of variations. Figures 47 through 49 present typical gas chromatograms obtained for the analysis of cryogenic traps (attenuation is constant).

Comparison of the absolute recoveries (Table 37) obtained in the absence of inorganic gases with the "high level" storage-stability study reveals that use of liquid O_2 as the coolant was more efficient than with powdered dry ice. However, the recoveries are still unacceptably low.

Figures 50 through 52 present examples of chromatograms for the "low level" interference study using cryogenic traps.

Because of the poor recoveries of Group I compounds using Ni traps packed with glass beads and liquid oxygen as the coolant, no recovery experiments with Group II compounds were conducted.

DISCUSSION

Containers

Bags--

Bags have the advantage of allowing collection of 10-100 liters of sample but they are easily punctured and clear bags must be protected from light after sample collection. Thorough cleaning can be complicated as the bags cannot be heated. Cleaning with ozone and/or ultraviolet light appears to reduce the levels of high boiling contaminants; actually these cleaning procedures may be producing compounds which are much less volatile or adsorb more strongly than the parent compounds.

Table 39. RELATIVE PERCENT RECOVERY OF GROUP I COMPOUNDS USING CRYOGENIC TRAPS IN THE INTERFERENCE STUDY[a]

Compound	Low Level Mean ± S.D. (C.V.)	High Level Mean ± S.D. (C.V.)
Vinyl chloride	96 ± 125 (130)	T
Methyl bromide	51 ± 56 (102)	T
Furan	ND[b]	ND
Acrylonitrile	I	I
Chloroprene	69 ± 48 (66)	ND
Chloroform	52 ± 25 (48)	21 ± 19 (93)
Benzene	52 ± 41 (80)	51 ± 53 (105)
1,2-Dichloropropane	42 ± 22 (52)	114 ± 67
Toluene	57 ± 29 (51)	62 ± 37 (60)
Tetrachloroethylene	51 ± 28 (55)	93 ± 41 (45)
Chlorobenzene	51 ± 15 (29)	92 ± 32 (35)
1,1,2,2-Tetrachloroethane	39 ± 24 (61)	119 ± 28 (24)
Bis-(2-chloroethyl)ether	54 ± 30 (56)	140 ± 25 (18)
m-Dichlorobenzene	52 ± 13 (25)	201 ± 42 (21)

[a] Relative recoveries were calculated between absolute recovery with no inorganic gases and inorganic gases. See Table 10 for levels of inorganic substances employed.

[b] ND = not detected, BI = background interference, T = trace.

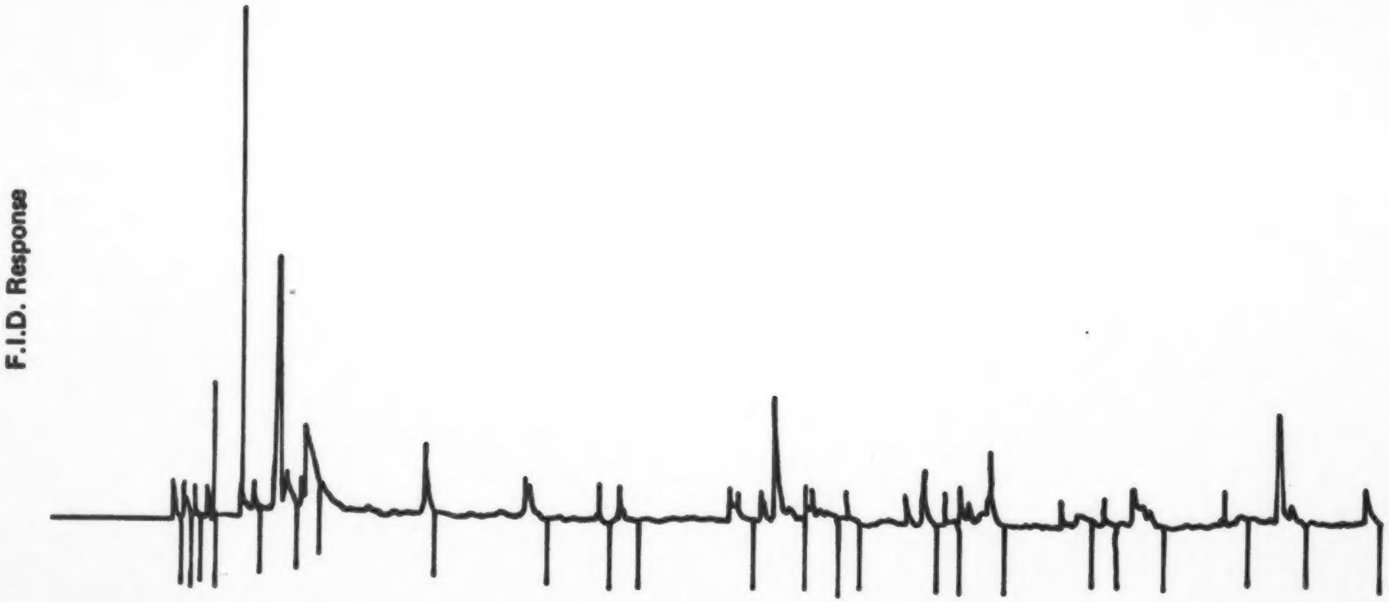

Figure 47. Chromatograms of background for cryogenic trap for 30 L of air sample containing high levels of inorganics and no test compounds.

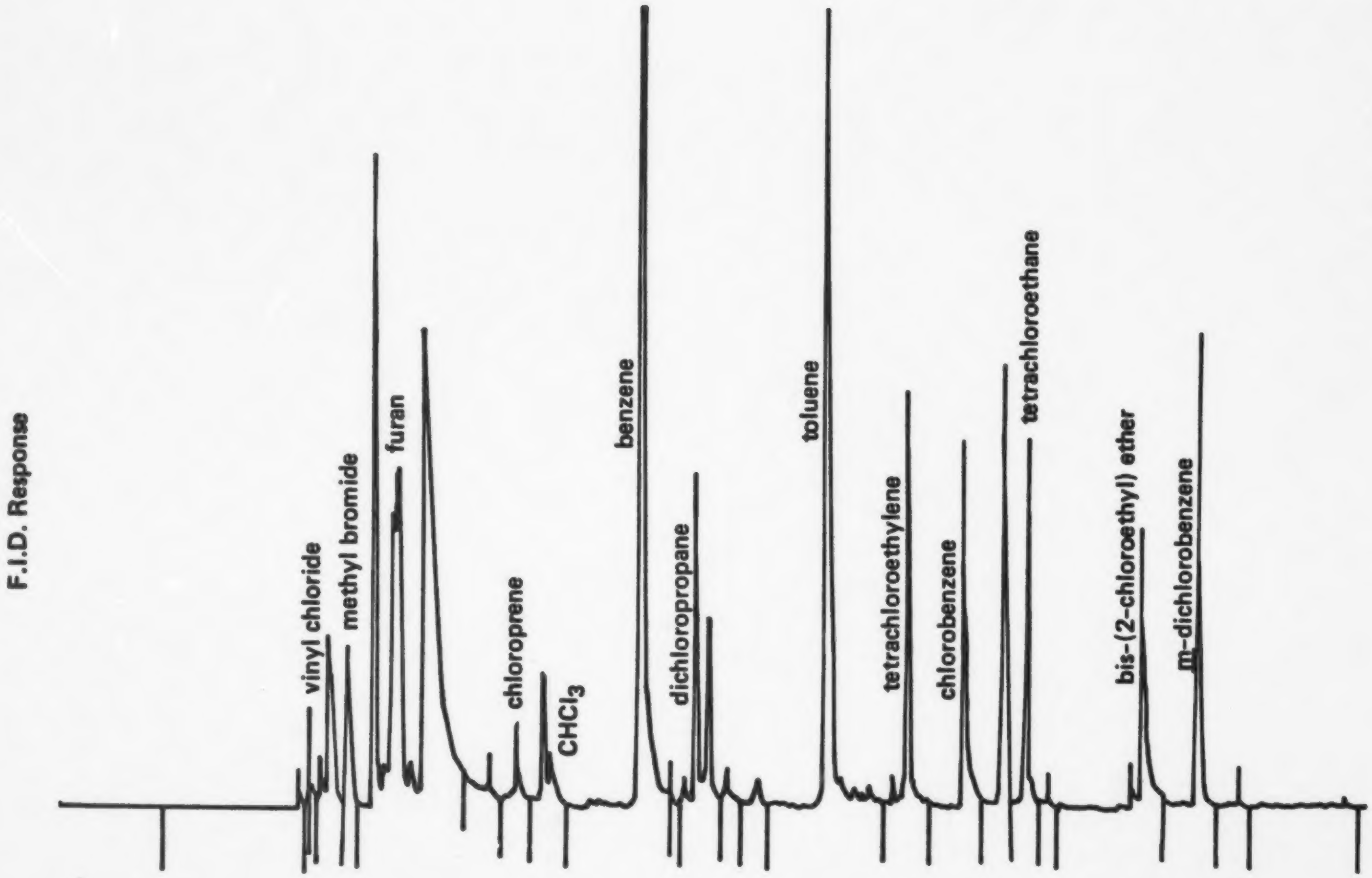

Figure 48. Chromatogram of sample collected with cryogenic trap without inorganics (high level study) and test compounds present.

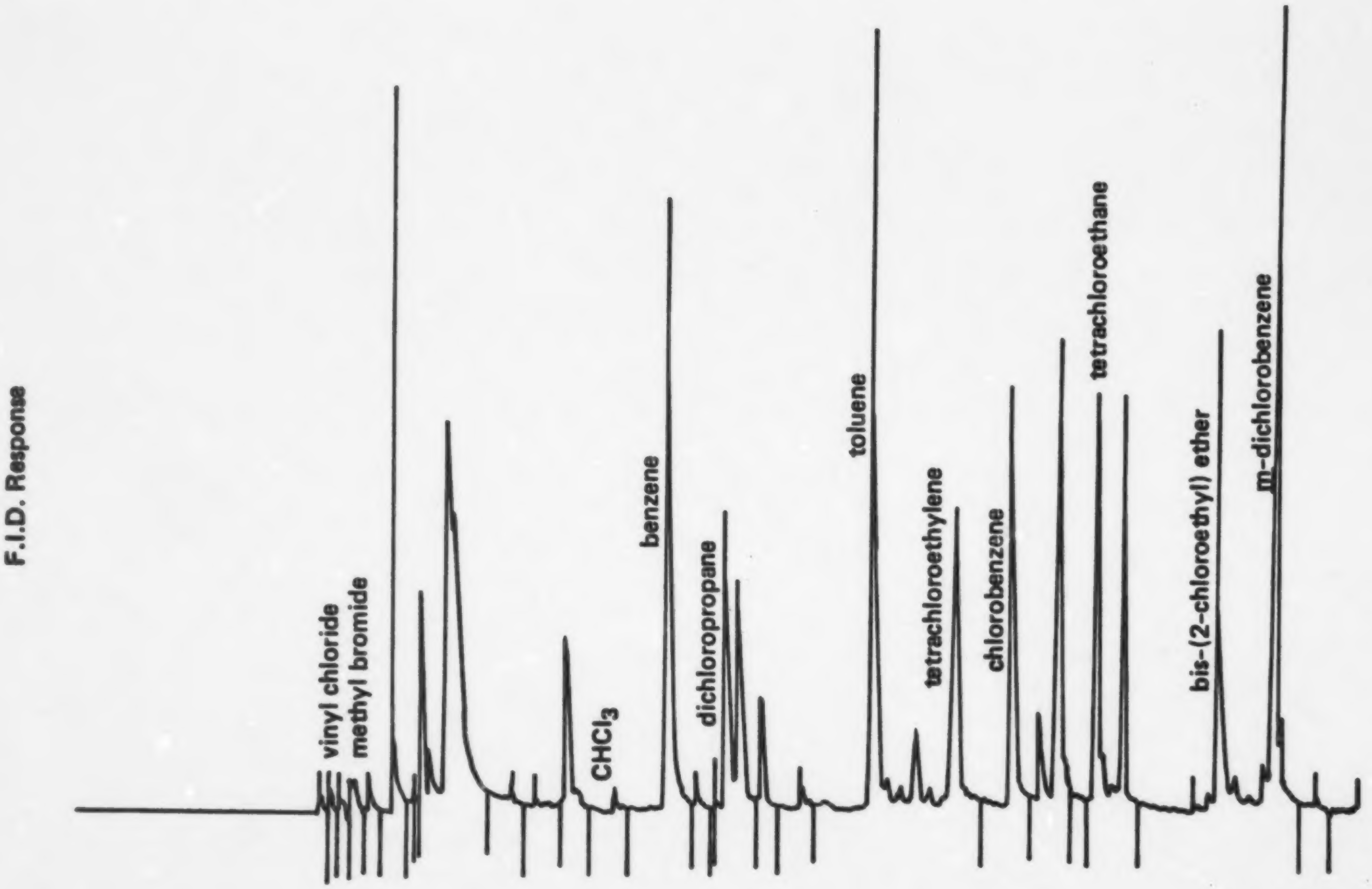

Figure 49. Chromatogram of sample collected with cryogenic trap with high levels of inorganic and test compounds present.

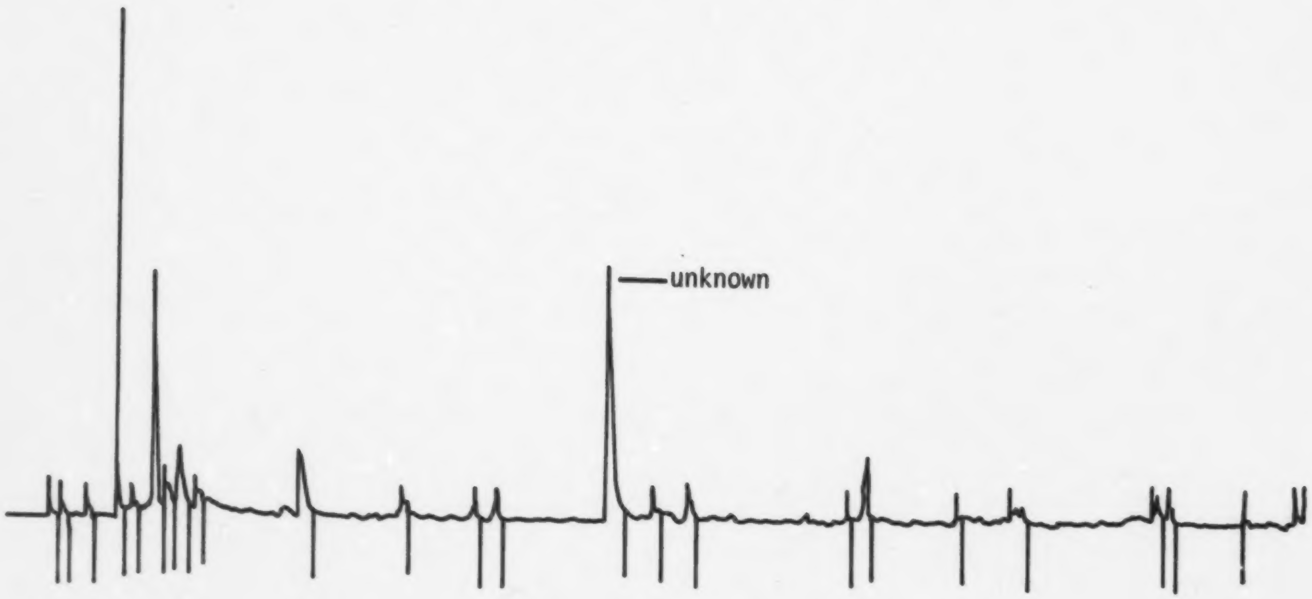

Figure 50. Chromatogram of background for cryogenic trap with low levels of inorganic gases and no test compounds.

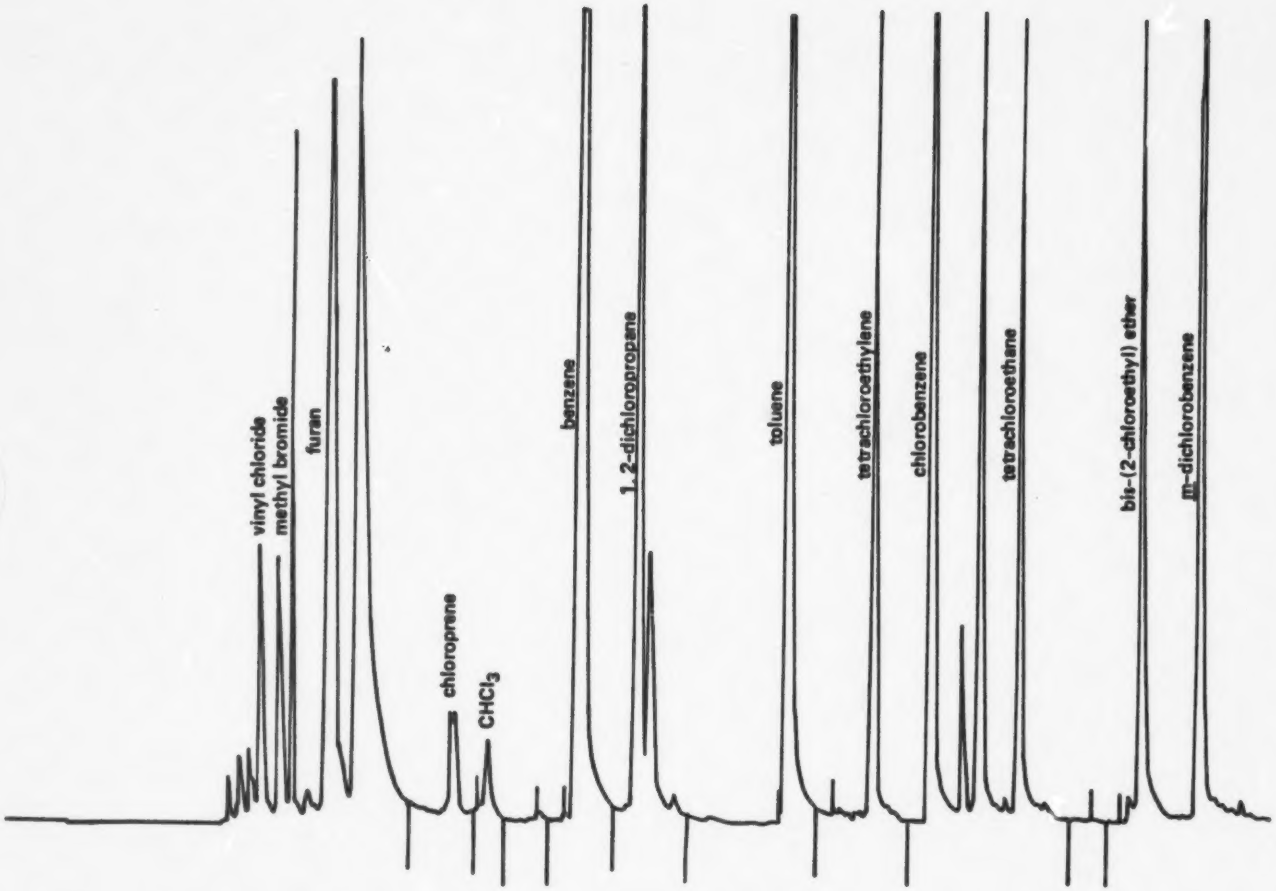

Figure 51. Chromatogram of sample collected with cryogenic trap with test compounds only (low level interference study).

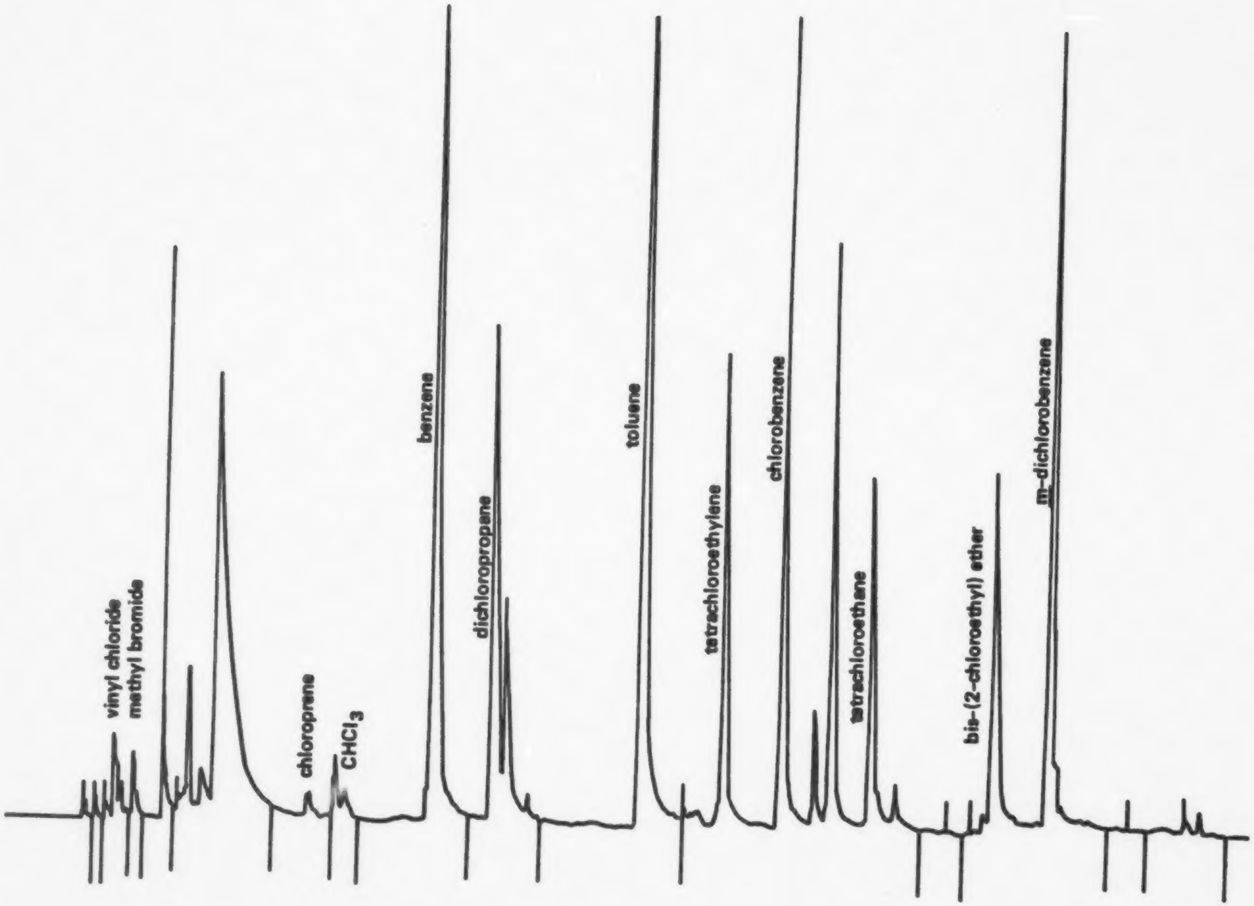

Figure 52. Chromatogram of sample collected with cryogenic trap with low level inorganic gases and test compounds present.

Recoveries from Teflon® and Tedlar® bags are generally similar shortly after sampling. However, with time, the decrease in recovery is generally more rapid with Teflon® than with Tedlar®. Both types of bags show both loss of compounds and influx of contaminants by permeation through the bag walls. It would seem that the aluminum coated bags should prevent this permeation; we could not test this possibility as we were unable to satisfactorily clean the aluminum coated bags. It appears than that bags not having sealed surfaces or not stored in clean environments should be trusted no more than 4-24 hours (depending on the levels of contaminants in the bag storage area) after sample collection.

The interferences decreased the recovery of most test compounds from the Tedlar® bags though a few compounds such as tetrachloroethylene and chlorobenzene showed an increase in recovery over that obtained in the absence of interferences. This increase may have been due to the water vapor blocking adsorption of and/or displacing already adsorbed organic molecules. One adverse effect caused by the interferences was the release of unknown contaminants from the wall of the Tedlar® bags.

Glass Bulbs--

The amount of sample which can be collected in a glass bulb is limited; usually 1-2 liters are available for analysis after collection. Glass bulbs are easily broken, especially the filling tube/valve part of the bulb. The bulbs should also be protected from light after sample collection. Bulbs can be cleaned by evacuation; heating while evacuating improves the efficiency of the cleaning process though care should be taken not to heat the valve. Cleaning with a solution is very difficult and time consuming since the valve must be disassembled, this latter operation leads to a high incidence of breakage.

The recovery of the test compounds from the glass bulbs decreased rapidly with increased boiling point and was above 90% for only a few compounds. The low level interferences increased the recoveries of many of the compounds above those obtained in the absence of interferences. The high levels of interferences generally decreased the recoveries over those obtained with low level interferences. The relatively high recoveries obtained in the presence of the interferences may well be due to the rapid occupation of sorption sites by water molecules, which prevents loss to the glass surface.

Steel Containers--

As with glass containers, steel containers allow recovery of only limited sample volumes, typically 4-6 liters. They are, however, extremely rugged and can be cleaned thoroughly by heating while evacuating.

The "Summa" polished containers generally show higher recovery for high boiling point compounds than the RTI-electropolished containers. Also the "Summa" electropolished containers show a better maintenance of recovery with time than the RTI-electropolished containers. As with bags, some test compounds show an actual increase in recovery from Day 3 to Day 7. This may well be due to the relatively slow displacement of organic molecules by water molecules in the test mixtures from the steel surface; this process would be expected to be slow in the test mixture as the water level is low in this case.

The low level interferences do not decrease recoveries but usually increase them. High level interferences increase recoveries for some compounds and decrease recoveries for others. These increases may be due to further displacement by water of the test compounds and/or release of contaminants not released during cleaning.

Detection Limits--

A limitation of cannisters (and bulbs) is their small volume, generally 2-9 liters. Even if a cannister is pressurized to two atmospheres, only two 1 liter samples can be acquired practically using the trapping and measurement system described previously. This is, of course, much less than the 10 liters than can be taken from a bag or the 50 liters that can be passed through a trap, Tenax, for example. The small volume that can be taken from a rigid cannister will lead to higher detection limits when compared to other bags or traps. This concern was tested using the cryogenic trapping and measurement system described and FID detection. Calibration mixtures at the 10 ppt and 1 ppb level were loaded into 2 L cannisters and then measured. Estimates of detection limits were calculated based on peak heights (2 chart divisions) and computer-calculated area counts (50 area counts) - two chart divisions and 50 area counts were assumed to be distinguishable from background signals. The detection limits are shown in Tables 40 and 41. The only compounds detected at the lower level were furan and toluene. This is to be expected; calculations from the higher level indicate that furan and toluene are the only compounds present in the low level calibration at greater than or near their minimum detection level.

Precision--

As stated previously, very few if any trends in precision are observed. The only significant trend seem to be a decrease in precision with storage time for some compounds. The precision decrease is more pronounced with the bags and steel containers relative to the glass bulbs. This may be related to the apparent rapid interaction between water and glass and the relatively slow interaction between water and plastic or steel.

Traps

Charcoal Cartridges--

The charcoal cartridges evaluated in this program for applicability to the collection of environmental levels of vapor-phase organics are widely used for industrial workplace monitoring. They have been endorsed by NIOSH for this purpose; however, their sampling requirements are significantly different since ppm levels are sought in the absence of ozone. As such 200 mg charcoal cartridges have not been adequately studied for environmental applications.

The limits of applicability of charcoal cartridges are revealed in the overall poor recovery and detection of organics. For the analysis of test compounds used in this study, GC/FID and GC/ECD were employed. An examination of the limits of detection for GC/FID indicated that none of the test compounds collected in the ppb range and a 30 L sample volume would be detected (Table 42). In fact, the chemicals were barely detectable in the calibration standard prepared at a concentration expected in the "high" level storage-stability study. When a selected number of T_0 cartridges were solvent desorbed and analyzed no chromatographic peaks were detected.

Sampling volumes larger than 30 L were not investigated. Presumably, volumes of 300 L or greater would be necessary to detect chemicals in the low ppb level. However, factors such as the breakthrough volume for the more volatile chemicals may prohibit adequate collection.

Table 40. PEAK HEIGHT CALCULATIONS

Compound	Calculated Concentration in S.S. can (ppt)	Peak Height (Chart Division)	Minimum Detectable Concentration Based on 2 Chart Divisions (ppt)
High Level (∼1 Part-Per-Billion)			
Toluene	887	20,21,21	85.8
m-Dichlorobenzene	814	6,7,8	233
1,2-Dichloropropane	1220	2,5,3,3	914
Furan	3630	51,47,46	151
1,1,2,2-Tetrachloroethane	2350	8,7,8	613
Low Level (∼100 Part-Per-Trillion)			
Toluene	88	1.5,1.3,2	110
m-Dichlorobenzene	81	N.D.	>81
1,2-Dichloropropane	120	N.D.	>120
Furan	359	5,5,3.5	160
1,1,2,2-Tetrachloroethane	232	N.D.	>232

N.D. = Not detected.

Table 41. AREA COUNT CALCULATION

Compound	Calculated Concentration in S.S. can (ppt)	Computer Calculated Area Counts	Minimum Detectable Concentration Based on 2 Chart Divisions (ppt)
High Level (∼1 Part-Per-Billion)			
Toluene	887	636,640,639	69
m-Dichlorobenzene	814	34,N.D.,238	171
1,2-Dichloropropane	1220	N.D.	>1220
Furan	3630	1211,1206,1117	154
1,1,2,2-Tetrachloroethane	2350	191,182,204	610
Low Level (∼100 Part-Per-Trillion)			
Toluene	88	N.D.	>88
m-Dichlorobenzene	81	N.D.	>81
1,2-Dichloropropane	120	N.D.	>120
Furan	359	121,164,168	119
1,1,2,2-Tetrachloroethane	232	N.D.	>232

N.D. = Not detected.

Table 42. CALCULATED CONCENTRATION OF TEST COMPOUNDS IN SOLVENT MIXTURE USED TO DESORB NIOSH CHARCOAL TUBES[a] - HIGH LEVEL STUDY

Compound	Maximum Wght. Collected (ng)	Concentration in $MeOH/CS_2$[b] (ng/μℓ)
Vinyl chloride	3,672	3.67
Methyl bromide	5,587	5.59
Acrylonitrile	6,054	6.05
Furan	8,340	8.34
Chloroprene	487	0.49
Chloroform	2,196	2.20
Benzene	5,742	5.74
1,2-Dichloropropane	3,326	3.33
Toluene	2,714	2.71
Tetrachloroethylene	6,102	6.10
1,1,2,2-Tetrachloroethane	8,438	8.44
Chlorobenzene	2,346	2.35
Bis-(2-chloroethyl)ether	8,410	8.41
m-Dichlorobenzene	3,606	3.61

[a] Based upon 30 L collection of ppb vapors from permeation/dilutor system.

[b] 1.0 ml solvent mixture was used to desorb charcoal.

On the other hand, GC/ECD did possess the inherent sensitivity to detect seven of the chemicals in Table 42. In fact, five of the chemicals possess a sufficient high electron affinity (21) to be detected in a 30 L sample of ppt levels.

The recovery of chemicals measurable by ECD was in general poor. The precision was erratic which prohibited the establishment of storage characteristics. Their evaluation was terminated with the "high" level interference experiments with Group I compounds.

Cryogenic Traps--

Initial storage-stability studies with empty cryogenic traps constructed of nickel and cooled with dry ice yielded poor recoveries for all chemicals at the ppb level. The cryogenic traps filled with clean glass beads (cryogen-dry ice) gave better recoveries for a few chemicals at the ppt level; however, the background was too elevated to measure accurately most of the chemicals. At neither level were the more volatile chemicals detected.

In subsequent experiments involving potential interferences from inorganic gases, liquid oxygen was used to cool nickel traps containing glass beads. Most compounds were detected, but the recoveries were still low and the precision was poor.

The applicability of cryogenic traps of the design evaluated in this study is limited. Because this method is labor intensive during sample collection, sample transport and storage (requiring continual cryogen), and sample recovery and analysis it is not a highly regarded technique. Substantial quantities of water accumulate during sampling and must be removed prior to sample analysis. Nafion® tubing has been used to remove water; however, polar substances are also lost (23).

The cryogenic trap theoretically has merits; particularly for very volatile substances. Further work is needed in an optimal design and addressing the inherent problems of atmospheric sampling.

Tenax® GC Cartridges--

The Tenax® GC cartridge is limited principally by the breakthrough volume which directly determines the detection limits attainable for a given measurement technique. In this study it was limited by the 30 L sampling volume for chemicals with breakthrough volumes less than this. Similarly the collection efficiency is directly related to the breakthrough volume.

Recoveries of chemicals were not significantly decreased by the short term storage (7 days); in fact storage of 2 to 3 months has been demonstrated in other studies (22). Precision of recoveries was slightly less than those observed for containers; however, with Tenax® GC cartridges the recovery was based upon triplicate sample analysis and not measurement of the same sample.

A major attribute of a cartridge sampling concept is its simplicity and convenience in preparation, sampling, transport, and recovery and analysis. Large numbers of samples can be taken simultaneously, stored until analysis and analyzed relatively rapidly. Cartridges must, however, be protected from sunlight.

Experiments with potential inorganic gas interferences readily demonstrated a major problem which can occur with any collection device. Reactive inorganic gases in the atmosphere can perturb the quantitative and qualitative composition of the air sample during collection of organics. Substantial improvement without adsorption losses can be attained by using a very small amount of mild reducing agent to remove ozone prior to trapping.

SECTION 7

SUPPORT AND QUALITY CONTROL DATA

SUPPORTING INFORMATION

Chromatographic Data

Analysis of Compounds from Cannisters--

The permeation tubes used to generate the test mixtures were placed in the permeation/dilution system in small groups; samples were then taken and analyzed. Using elution orders established by earlier Tenax studies (see below) the GC peaks for the various compounds were verified.

Analysis of Compounds from Tenax® GC Cartridges--

The retention times for authentic compounds employed in this research program were established and divided into two groups for conducting the storage-stability and interference studies. These data for thermal desorption glass capillary gas chromatographic analysis are given in Tables 43 and 44.

Analysis of Compounds from Charcoal Cartridges--

The compounds adsorbed to charcoal cartridges were recovered by solvent desorption and microliter aliquots were analyzed by GC with flame ionization and electron capture detection. The retention data which were established by injection of authentic compounds are given in Tables 45 and 46. Charcoal cartridges were not evaluated with the Group II compounds.

Calibration Data

Analysis of Compounds from Cannisters--

The FID response was standardized at three different compound concentrations by drawing a sample directly from the glass manifold through a heated 1/8" o.d. stainless steel tube into the GC sampling system. Each concentration generated was calculated based upon the permeation rate of the compound, the dilution air flow, and the volume of sample trapped-out. The

Table 43. RETENTION TIMES FOR GROUP I COMPOUNDS ANALYZED BY TD/HRGC[a]

Compound	Retention Time ± S.D. (C.V.) (min)
Vinyl chloride	4.99 ± 0.035 (0.7)
Methyl bromide	5.65 ± 0.023 (0.4)
Furan	6.88 ± 0.058 (1.2)
Acrylonitrile	7.95 ± 0.072 (0.9)
Chloroprene	10.71 ± 0.055 (0.5)
Chloroform	11.81 ± 0.030 (0.2)
Benzene	14.38 ± 0.084 (0.5)
1,2-Dichloropropane	16.34 ± 0.015 (0.09)
Toluene	20.81 ± 0.091 (0.4)
Tetrachloroethylene	24.43 ± 0.010 (0.04)
Chlorobenzene	25.20 ± 0.050 (0.02)
Tetrachloroethane	27.92 ± 0 (0)
Bis-(2-Chloroethyl)ether	31.82 ± 0.023 (0.07)
m-Dichlorobenzene	33.39 ± 0 (0)
1,2,3-Trimethylbenzene	34.39 ± 0.010 (0.02)

[a] See Table 8 for operating parameters.

Table 44. RETENTION TIMES OF GROUP II COMPOUNDS ANALYZED BY TD/HRGC[a]

Compound	Retention Time (min)	Temp. (°C)
Methyl chloride	6.60	10.4
Propylene oxide	8.80	19.2
Vinylidene chloride	9.56	22.2
Allyl chloride	10.05	24.2
1,1,1-Trichloroethane	15.13	44.5
α-Epichlorohydrin	18.65	58.6
Methyl mercaptan	20.23	64.9
Ethylbenzene	26.97	91.9
o-Xylene	28.59	98.4
Benzyl chloride	33.92	120
n-Decane	34.61	122
1,2,3-Trimethylbenzene	35.04	124
o-Cresol	36.08	128
Nitrobenzene	37.15	133

[a] See Table 8 for operating parameters, mean of three determinations.

Table 45. RETENTION CHARACTERISTICS OF MODEL COMPOUNDS RECOVERED FROM CHARCOAL CARTRIDGES AND ANALYZED BY GC/FID[a]

Compound	Retention Time (Min)	Temperature (°C)
Acrylonitrile	4.0	50
Furan	4.8	50
Chloroform	9.6	70
Chloroprene	16.0	110
1,2-Dichloropropane	16.5	113
Benzene	19.2	130
1,1,2,2-Tetrachloroethane	24.6	160
Tetrachloroethylene	25.8	168
Toluene	27.6	180
Chlorobenzene	28.8	186
Bis-(2-chloroethyl)ether	29.2	190
m-Dichlorobenzene	36.8	210
1,2,3-Trimethylbenzene	46.5	210

[a] Chromatographic conditions were given in Table 9, mean of three determinations.

Table 46. RETENTION TIMES OF MODEL COMPOUNDS RECOVERED FROM CHARCOAL CARTRIDGES AND ANALYZED BY GC/ECD[a]

Compound	Retention Time (min)
Chloroform	2.0
Chloroprene	3.2
1,2-Dichloropropane	3.7
1,1,2,2-Tetrachloroethane	11.5
Tetrachloroethylene	13.5
Bis-(2-chloroethyl)ether	22.5

[a] Operating parameters were given in Table 9, mean of three determinations.

concentrations used in establishing a standard curve and the correlation coefficient for each curve are given in Table 47.

Tables 47 and 48 give the calibration data for Group I and Group II compounds, respectively. Using a four point calibration (including zero) a linear regression was established. Table 49 gives calibration data for Group I compounds in the interference study. The interference study for Group II compounds was performed immediately following the storage stability study for Group II compounds. A calibration check showed no change in the GC system response to standards and so the data presented in Table 48 was used as calibration data for the interference study with Group II compounds. The correlation coefficients for each compound are also provided. Each measurement was performed in triplicate.

Analysis of Compounds from Tenax® GC Cartridges--

The absolute retention times for model compounds were determined on an SE-30 SCOT column (Table 8).

In order to determine the quantities of each of the compounds collected on the sampling devices, the gas chromatographic system was calibrated in the range that was anticipated to be collected at the low level and essentially consisted of an extension of the standard curve for each of the compounds at the high level. The procedures for calibrating the gas chromatographic system were identical to that described for the high levels employing both permeation tube and a flash unit for cross-checking the slope of the standard curves.

Table 50 presents the results of instrumental calibration for Tenax cartridge analysis (high level). Except for one case, the correlation coefficients of the standard curves were 0.99, while for acrylonitrile it was 0.92. A small background peak reduced the accuracy of the standard curve for acrylonitrile.

The calibration results for the low level studies are given in Table 51. Only those compounds which were detected in the low level study are indicated. The mass range simply was an extension of the high level calibration. The area obtained, standard deviation and coefficient of variation for triplicate analysis at each mass are presented. Correlation coefficients and slopes were calculated for the linear regression data. Except for

Table 47. GROUP I COMPOUND CALIBRATION DATA FOR BAGS, BULBS AND CANNISTERS
FEBRUARY, 1981

Compound	Concentrations, ppb	Correlation Coeff.
Vinyl chloride	34, 18, 11	0.999
Methyl bromide	86, 45, 29	0.999
Furan/acrylonitrile	170, 89, 57	0.998
Chloroprene	6.2, 3.2, 2.1	0.999
Chloroform	17, 8.9, 5.8	0.995
Benzene	64, 33, 22	0.999
1,2-Dichloropropane	30, 16, 10	0.999
Toluene	27, 14, 9.0	0.998
Tetrachloroethylene	33, 17, 11	0.998
Chlorobenzene	19, 10, 6.5	0.998
1,1,2,2-Tetrachloroethane	40, 21, 14	0.998
Bis(2-Chloroethyl)ether	23, 12, 7.8	0.999
1,2,3-Trimethylbenzene	113, 59, 38	0.999
m-Dichlorobenzene	22, 11, 7.4	0.999

Table 48. GROUP II COMPOUND CALIBRATION DATA FOR BAGS, BULBS AND CANNISTERS
JUNE, 1981

Compound	Concentrations ppb	Correlation Coefficient
Methyl chloride	223,112,56.6	0.999
Propylene oxide[a]	---	---
Vinylidene chloride	82.6,41.4,20.9	0.999
Allyl chloride	361,181,91.4	0.999
1,1,1-Trichloroethane	41.9,25.6,12.8	0.999
α-Epichlorohydrin[a]	---	---
Methyl mercaptan[c]	118,59.0	---
Ethylbenzene	29.8,14.9,7.5	0.998
o-Xylene	68.7,42.0,21.0	0.999
Benzyl chloride	116,57.9,29.2	0.997
n-Decane	30.8,15.4,7.8	0.998
1,2,3-Trimethylbenzene	234,143,71.5	0.999
o-Cresol[b]	---	---
Nitrobenzene[c]	53.9,27.2	---

[a] Not detected in sample containers and poor integration in standards.

[b] Not detected in standard or sample containers.

[c] Two point calibration - non-linear response at high concentrations.

Table 49. GROUP I COMPOUND CALIBRATION DATA WITH BAGS, BULBS AND CANNISTERS FOR INTERFERENCE STUDIES JULY, 1981

Compound	Concentrations (ppb)	Correlation Coefficient
Vinyl chloride	52.8,38.6,27.7,13.9	0.999
Methyl bromide	114.5,83.8,60.1,30.1	0.999
Furan/Acrylonitrile[a]		
Chloroprene[b]		
Chloroform[b]		
Benzene	61.7,45.2,32.4,16.2	0.999
1,2-Dichloropropane	33.3,24.4,17.5,8.8	0.995
Toluene	25.9,19.0,13.6,6.8	0.992
Tetrachloroethylene[c]	17.3,12.4,6.2	0.999
Chlorobenzene[c]	12.8,9.2,4.6	0.997
1,1,2,2-Tetrachloroethane	35.2,25.8,18.5,9.3	0.993
Bis-(2-chloroethyl)ether	4.6,3.3,2.4,1.2	0.999
m-Dichlorobenzene	21.0,15.3,11.0,5.5	0.984

[a] Based on furan only, acrylonitrile tube polymerized.

[b] Not quantified due to interfering peaks.

[c] Three-point calibration - non-linear response at high concentration.

Table 50. GROUP I COMPOUND CALIBRATION DATA FOR TENAX CARTRIDGE ANALYSIS - HIGH LEVEL

Methyl bromide	424	10.87 ± 0.94 (8.6)	0.99
	851	18.73 ± 0.55 (2.9)	
	1273	27.53 ± 1.26 (4.6)	
Vinyl chloride	100	5.68 ± 0.76 (13.4)	0.99
	200	9.10 ± 0.86 (9.4)	
	300	14.57 ± 0.58 (3.9)	
Benzene	139	37.48 ± 2.94 (7.8)	0.99
	208	58.03 ± 1.65 (2.8)	
	277	80.96 ± 0.25 (0.3)	
Chloroform	100	2.94 ± 0.15 (5.1)	0.99
	200	4.79 ± 0.10 (2.1)	
	300	6.69 ± 0.76 (11.4)	
Toluene	68	25.40 ± 2.02 (7.9)	0.99
	102	28.99 ± 2.53 (8.7)	
	135	37.26 ± 1.44 (3.9)	
1,2,3-Trimethylbenzene	226	19.95 ± 1.05 (5.3)	0.99
	451	44.07 ± 1.28 (2.9)	
	902	90.97 ± 2.42 (2.7)	
Furan	200	22.28 ± 2.46 (11.0)	0.99
	300	32.55 ± 2.18 (6.7)	
	400	53.26 ± 1.44 (2.9)	
Bis(2-Chloroethyl)ether	449	0.34 ± 0 (0)	0.99
	903	0.62 ± 0.04 (6.8)	
	1797	1.25 ± 0.12 (9.6)	
1,1,2,2-Tetrachloroethane	417	100.42 ± 4.19 (4.8)	0.99
	627	155.86 ± 11.89 (7.6)	
	835	213.22 ± 3.71 (3.7)	
	1671	455.38 ± 12.24 (2.7)	
Acrylonitrile	145	11.46 ± 0.86 (7.5)	0.92
	217	13.16 ± 2.34 (17.8)	
	289	33.33 ± 4.76 (14.3)	
Tetrachloroethylene	303	96.96 ± 5.50 (5.7)	0.99
	455	148.81 ± 11.58 (7.8)	
	607	198.46 ± 4.66 (2.3)	
	1217	430.72 ± 7.83 (1.8)	

(continued)

Table 50 (cont'd.)

Compound	Mass (ng)	Area ± S.D. (C.V.) (mean)	Correlation Coefficient
1,2-Dichloropropane	166	16.24 ± 0.17 (1.0)	0.99
	250	25.54 ± 0.80 (3.2)	
	333	36.54 ± 2.23 (6.1)	
	666	72.24 ± 1.99 (2.7)	
Chlorobenzene	104	17.02 ± 1.20 (7.0)	0.99
	208	32.19 ± 0.56 (1.7)	
	311	48.88 ± 2.62 (5.4)	
m-Dichlorobenzene	166	21.40 ± 1.84 (8.6)	0.99
	333	38.03 ± 0.89 (2.3)	
	498	58.12 ± 3.87 (6.7)	
Chloroprene	50	5.02 ± 0.73 (14.5)	0.99
	100	8.58 ± 1.12 (13.0)	
	200	15.89 ± 1.34 (8.4)	

[a] Permeation tubes were used.

Table 51. GROUP I COMPOUND CALIBRATION DATA FOR TENAX CARTRIDGE ANALYSIS - LOW LEVEL[a]

Compound	Mass (ng)	Area ± S.D. (C.V.) (mean)	Correlation Coefficient	Slope
Benzene	28	4.30 ± 0.87 (20)	0.99	0.200
	100	20.64 ± 2.49 (12)		
	192	37.04 ± 3.21 (9)		
1,2-Dichloropropane	22	1.20 ± 0.05 (4)	0.99	0.062
	81	4.55 ± 0.46 (10)		
	155	9.62 ± 0.52 (5)		
Toluene	14	0.72 ± 2.98 (412)	0.98	0.310
	48	9.60 ± 3.82		
	92	27.74 ± 3.89 (14)		
Tetrachloroethylene	30	0.55 ± 0.24 (44)	0.99	0.037
	105	3.26 ± 0.30 (9)		
	201	11.83 ± 1.02 (9)		
Chlorobenzene	12	0.93 ± 0.38 (41)	0.99	0.150
	42	5.75 ± 0.95 (17)		
	80	11.83 ± 1.02 (9)		
1,1,2,2-Tetrachloroethane	64	1.16 ± 0.12 (10)	0.99	0.017
	231	4.45 ± 0.38 (9)		
	443	7.28 ± 0.61 (8)		
Bis-(2-Chloroethyl)ether	-		-	-
	139	3.50 ± 0.31 (9)		
	267	12.62 ± 1.57 (12)		
m-Dichlorobenzene	20	1.77 ± 0.60 (34)	0.99	0.130
	70	8.65 ± 0.67 (8)		
	135	16.69 ± 0.62 (4)		

[a] Permeation tubes were used.

toluene which had a correlation coefficient of 0.98, all of the remaining correlations were 0.99.

Data for Group II compounds are given in Table 52.

QUALITY CONTROL DATA

Preparation and Calibration of Permeation Tubes

During the course of this research project permeation tubes were prepared for the model compounds of interest, some of which are listed in Table 53 with construction materials and dimensions. In order to access the range of permeation rates attainable, permeation tubes for each model compounds were prepared using three kinds of plastic tubing. Surgical grade polyethylene (PE) and two types of Teflon®: tetrafluoroethylene (TFE) and perfluoroethylenepropylene (FEP). The lengths varied from a few mm to 15 cm. The ends were sealed with glass plugs secured by stainless steel ferrules. This technique proved useful since a vapor pressure well above one atmosphere for dimethylamine could be easily contained.

The selection of the appropriate plastic tubing for organics becomes a facile process once the behavior of a few compounds for a chemical class is known. In general, the non-polar liquids/gases are prepared in the Teflon® tube while the more polar, lesser volatile materials permeate at the desired rate in polyethylene.

In previous studies it was determined that permeation systems at 20°C resulted in severe adsorptive/condensation losses; thus all permeation tubes were equilibrated at 30°C.

The permeation tubes were gravimetrically calibrated on a bi-weekly schedule using a Mettler MS-5A (microgram) or Cahn balance.

Permeation tubes which were periodically gravimetrically calibrated were used throughout all studies to synthesize air-vapor mixtures and for calibrating instruments. Historical records of the permeation rates experienced during the storage-stability and interference studies are given in Tables 54 and 55. Each permeation rate represents a linear regression analysis of at least five previous weighings. The mean, standard deviation and coefficient of variation are also indicated.

The permeation rates for most of Group I compounds were stable with coefficient of variations under 10% during the 11 month period.

Table 52. GROUP II COMPOUND CALIBRATION DATA FOR TENAX CARTRIDGE ANALYSIS[a]

Compound	Mass (μg)	Area: Mean ± S.D. (C.V.)	Slope	Correlation Coefficient
Methyl chloride	583	102 ± 23 (23)	0.953[b]	0.953[b]
	2,915	405 ± 81 (2)		
	5,830	504 ± 174 (35)		
Propylene oxide	239	202 ± 50 (25)	0.505	0.976
	1,036	657 ± 116 (18)		
	1,915	1,050 ± 87 (8.3)		
Vinylidene chloride	294	245 ± 19 (7.7)	0.452	0.972
	1,273	733 ± 110 (15)		
	2,351	1,176 ± 152 (13)		
Allyl chloride	1,116	719 ± 59 (8.2)	0.520	0.995
	4,830	2,913 ± 139 (4.8)		
	8,925	4,790 ± 210 (4.4)		
1,1,1-Trichloroethane	240	110 ± 5.6 (5.1)	0.424	0.962
	1,040	556 ± 8.6 (15)		
	1,922	826 ± 108 (13)		
α-Epichlorohydrin	907	290 ± 71 (24)	0.381	0.977
	3,919	1,775 ± 86 (4.8)		
	7,235	2,715 ± 293 (11)		
Methyl mercaptan	293	31.1 ± 3.2 (10)	0.115	0.933
	1,465	160 ± 43 (27)		
	2,930	333 ± 92 (28)		
Ethylbenzene	194	246 ± 48 (20)	1.015	0.992
	839	894 ± 15 (1.6)		
	1,549	1,620 ± 144 (8.9)		
o-Xylene	174	244 ± 12 (4.9)	1.236	0.991
	751	925 ± 23 (2.5)		
	1,386	1,740 ± 166 (9.5)		
Benzyl chloride	238	10.9 ± 9.5 (87)	0.236	0.737
	1,032	225 ± 169 (75)		
	1,907	362 ± 213 (59)		
n-Decane	263	234 ± 7.9 (3.4)	0.966	0.984
	1,136	962 ± 57 (5.9)		
	2,097	2,001 ± 242 (12)		

(continued)

Table 52 (cont'd.)

Compound	Mass (μg)	Area: Mean ± S.D. (C.V.)	Slope	Correlation Coefficient
1,2,3-Trimethylbenzene	1,038	847 ± 13 (1.5)	0.788	0.995
	4,492	3,401 ± 32 (0.9)		
	8,299	6,568 ± 479 (7.3)		
o-Cresol	582	65.1 ± 23.2 (36)	0.258	0.839
	2,518	759 ± 240 (32)		
	4,648	1,122 ± 504 (45)		
Nitrobenzene	397	745 ± 24 (3.2)	1.959	0.986
	1,716	3,377 ± 97 (2.9)		
	3,169	6,177 ± 775 (12.6)		

[a] Includes cryogenic traps; permeation tubes were used.

[b] Based on medium and low levels only.

Table 53. PERMEATION TUBES PREPARED AND AVAILABLE DURING THE PAST YEAR[a]

Compound	Polymeric Material	Dimensions (mm i.d. x mm length)	Supplier	Permeation Rate (μg/min)[b]
Chloroform	FEP	0.476 x 107	RTI	0.1569
1,1,2,2-Tetrachloroethane	PE	0.317 x 5	RTI	0.6388
1,2-Dichloropropane	TFE	0.476 x 77	RTI	0.2242
Vinyl chloride	TFE	-	Kin-Tek	0.2980
2-Chloro-1,3-butadiene	TFE	0.476 x 95	RTI	0.1346
Tetrachloroethylene	TFE	0.476 x 52	RTI	0.4335
Chlorobenzene	TFE	0.476 x 55	RTI	0.1617
m-Dichlorobenzene	TFE	0.476 x 60	RTI	0.2583
Benzene	TFE	0.476 x 125	RTI	0.5135
Toluene	TFE	0.476 x 70	RTI	0.1938
1,2,3-Trimethylbenzene	PE	0.317 x 8	RTI	0.3668
Acrylonitrile	TFE	0.476 x 48	RTI	0.4363
Furan	FEP	0.476 x 113	RTI	0.5928
Bis(2-chloroethyl)ether	PE	0.317 x 80	RTI	1.3020
Methyl bromide	TFE	0.476 x 50	Metronics	0.6700
1,1,1-Trichloroethane	TFE	0.476 x 80	RTI	0.0943
Methyl chloride	TFE	0.476 x 10	Metronics	0.4000
1,1-Dichloroethylene	TFE	0.476 x 101	RTI	0.0556
Benzyl chloride	PE	0.317 x 80	RTI	NE[c]
Propylene oxide	TFE	0.476 x 51	RTI	0.9364

(continued)

Table 53 (cont'd.)

Compound	Polymeric Material	Dimensions (mm i.d. x mm length)	Supplier	Permeation Rate (µg/min)[b]
1,4-Dioxane	TFE	0.476 x 102	RTI	0.0791
Phenol	PE	0.317 x 96	RTI	0.4337
o-Cresol	PE	0.317 x 109	RTI	0.7897
Acrolein	TFE	0.476 x 100	RTI	0.2692
Dimethylamine	FEP	0.476 x 70	RTI	0.2576
Di-*n*-butylamine	TFE	0.476 x 52	RTI	0.7289
Pyridine	TFE	0.476 x (?)	RTI	0.1339
Aniline	TFE	0.476 x 98	RTI	0.0492
t-Butyl mercaptan	TFE	0.476 x 74	RTI	0.0857
Nitrobenzene	PE	0.317 x 10	RTI	NE

[a] Listing includes those prepared through October, 1979.

[b] Rates are for 30°C.

[c] NE = not equilibrated.

Table 54. HISTORICAL RECORD OF PERMEATION RATES FOR GROUP I COMPOUNDS DURING STORAGE-STABILITY AND INTERFERENCE STUDIES[a]

	Month										
Compound	JAN (1980)	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV
Vinyl chloride	-	-	268[b]	268[b]	268 ± 5 (2)	268 ± 5 (2)	171[b,c]	171	171	171 ± 3 (2)	171
Methyl bromide	-	-	670[b]	670[b]	670 ± 5 (1)	670 ± 5 (1)	670 ± 5 (1)	670 ± 13 (2)	670 ± 13 (2)	670 ± 13 (2)	-
Furan	465 ± 17 (3.7)	471 ± 15 (3.2)	465 ± 10 (2.1)	465 ± 10 (2.1)	607 ± 16 (3)	605 ± 15 (2.5)	458 ± 9 (2)	455 ± 2 (0.4)	453 ± 4 (0.9)	449 ± 11 (2)	440 ± 10 (2.3)
Acrylonitrile	459 ± 47 (10)	432 ± 8.1 (1.9)	431 ± 10 (2.3)	431 ± 8.8 (2.0)	755 ± 36 (5)	431 ± 11 (2.5)	421 ± 5 (1)	420 ± 3 (0.7)	417 ± 8 (2)	413 ± 10 (2)	413 ± 9.8 (2.4)
Chloroprene	213[b]	226 ± 19 (8.4)	218 ± 31 (14)	216 ± 31 (14)	23 ± 2 (9)	175 ± 7 (4)	68[c]	16 ± 31 (194)	32 ± 33 (103)	32 ± 30 (94)	37 ± 4 (11)
Chloroform	154 ± 5 (3.2)	160 ± 4.3 (2.7)	162 ± 4.0 (2.5)	160 ± 4.2 (2.6)	160 ± 5 (3)	160 ± 4 (2.5)	158 ± 6 (3.8)	162 ± 6 (4)	161 ± 5 (3)	159 ± 7 (4)	163 ± 14 (8.5)
Benzene	418 ± 14.6 (3.5)	419 ± 13.9 (3.3)	420 ± 14.2 (3.4)	423 ± 2.1 (0.5)	420 ± 8 (2)	420 ± 14 (3)	418 ± 8 (2)	418 ± 8 (2)	419 ± 8 (2)	421 ± 7 (2)	422 ± 8.7 (2.1)
1,2-Dichloropropane	241 ± 60 (25)	264 ± 78 (29)	288 ± 76 (26)	332 ± 43 (13)	338 ± 41 (12)	287 ± 75 (26)	351 ± 18 (5)	352 ± 17 (5)	357 ± 27 (8)	344 ± 48 (14)	-[b]
Toluene	196 ± 8.4 (4.2)	196 ± 8.4 (4.3)	196 ± 7.5 (3.8)	200 ± 13 (6.5)	201 ± 13 (6)	196 ± 7 (3.5)	205 ± 10 (5)	207 ± 8 (4)	208 ± 8 (4)	206 ± 16 (8)	207 ± 16 (7.9)
Tetrachloroethylene	437 ± 19 (4.3)	442 ± 13 (2.9)	440 ± 6.5 (1.5)	441 ± 13 (2.9)	438 ± 18 (4)	445 ± 9 (2)	443 ± 14 (3.2)	434 ± 15 (3)	439 ± 25 (6)	450 ± 23 (5)	443 ± 42 (9.4)
Chlorobenzene	163 ± 28 (17)	164 ± 32 (19)	163 ± 14 (8.5)	173 ± 1.2 (1)	175 ± 6 (3)	175 ± 7 (4)	183 ± 16 (9)	186 ± 15 (8)	188 ± 14 (7)	189 ± 11 (6)	185 ± 10.7 (5.8)
1,1,2,2-Tetrachloroethane	608 ± 124 (20)	524 ± 28 (5)	545 ± 66 (12)	545 ± 60 (11)	968 ± 50 (5)	574 ± 99 (17)	183 ± 16 (9)	630 ± 60 (10)	562 ± 16 (3)	596 ± 63 (11)	596 ± 62 (10)
Bis-(2-chloroethyl)ether	-	584 ± 35 (6.0)	580 ± 26 (4.4)	584 ± 19 (3.2)	584 ± 10 (2)	580 ± 14 (2.4)	609[c]	586 ± 5 (0.9)	580 ± 16 (3)	532 ± 116 (21)	532 ± 113 (21)
o-Dichlorobenzene	256 ± 31 (12)	259 ± 28 (11)	254 ± 20 (7.8)	273 ± 46 (17)	294 ± 66 (22)	261 ± 25 (9.5)	314 ± 61 (19)	326 ± 50 (15)	327 ± 49 (15)	310 ± 57 (18)	-[b]

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[a] Permeation rates are derived from at least five gravimetric determinations (over prior 3 month period) and linear regression analysis - Mean (ng/min) ± S.D. (C.V.).

[b] Not statistically analyzed.

[c] New permeation tubes.

Table 55. HISTORICAL RECORD OF PERMEATION RATES FOR GROUP II COMPOUNDS DURING STORAGE-STABILITY AND INTERFERENCE STUDIES[a]

Compound	Month				
	JAN (1981)	FEB		MAR	
Methyl chloride	451[b]	451 ± 3.1 (0.7)	452 ± 3.2 (0.7)	456 ± 9.0 (2.0)	457 ± 9.2 (2.0)
Propylene oxide	270 ± 7.8 (2.9)[c]	267 ± 7.5 (2.8)[c]	264 ± 5.9 (2.2)[c]	264 ± 4.8 (1.8)	263 ± 4.6 (1.7)
Vinylidene chloride	-	-	-	-	153[b]
Allyl chloride	1,447 ± 64 (4.4)	1,413 ± 81 (5.7)	1,377 ± 82 (6.0)	1,343 ± 76 (5.6)	1,305 ± 58 (4.4)
1,1,1-Trichloroethane	263 ± 17 (6.4)	255 ± 15 (5.8)	249 ± 11 (4.3)	246 ± 7.2 (2.9)	254 ± 25 (9.8)
α-Epichlorohydrin	-	-	629[b]	696[b]	685 ± 51 ([illegible] 5)
Methyl mercaptan	-	529[b]	514[b]	513 ± 18 (3.4)	506 ± 20 (3.9)
Ethylbenzene	136 ± 4.9 (3.6)	136 ± 4.2 (3.1)	135 ± 5.8 (4.3)	135 ± 6.9 (5.1)	134 ± 7.3 (5.4)
o-Xylene	-	-	-	-	-
Benzyl chloride	243 ± 7.2 (3.0)	242 ± 8.5 (3.5)	242 ± 8.4 (3.5)	240 ± 7.4 (3.1)[c]	243 ± 12 (4.9)[c]
n-Decane	244 ± 44 (18)	233 ± 47 (20)	216 ± 42 (19)	204 ± 32 (16)	189 ± 19 (10)
1,2,3-Trimethylbenzene	1,099 ± 74 (6.8)	1,101 ± 73 (6.7)	1,101 ± 73 (6.7)	1,115 ± 64 (5.7)	1,106 ± 77 (6.9)
o-Cresol	554 ± 74 (13)	513 ± 69 (13)	483 ± 66 (14)	458 ± 61 (13)	438 ± 53 (12)
Nitrobenzene	276 ± 17 (6.2)	297 ± 57 (19)	292 ± 58 (20)	297 ± 55 (19)	294 ± 57 (19)

(continued)

Table 55 (Cont'd.)

Compound	Month			
	Apr		May	
Methyl chloride	459 ± 9.3 (2.0)	461 ± 8.5 (1.9)	464 ± 5.3 (1.1)	465 ± 3.0 (0.6)
Propylene oxide	264 ± 4.4 (1.7)	264 ± 4.6 (1.7)	263 ± 5.3 (2.0)	265 ± 6.6 (2.5)
Vinylidene chloride	316[b]	316[b]	323 ± 12 (3.9)[c]	326 ± 12 (3.5)[c]
Allyl chloride	1,275 ± 43 (3.4)	1,249 ± 43 (3.4)	1,226 ± 49 (4.0)	1,202 ± 51 (4.3)
1,1,1-Trichloroethane	263 ± 30 (11)	262 ± 30 (12)	264 ± 29 (11)	281 ± 41 (14)
α-Epichlorohydrin	645 ± 120 (19)[d]	603 ± 114 (19)[d]	557 ± 43 (7.8)[d]	578 ± 11 (2.0)[d]
Methyl mercaptan	498 ± 25 (5.1)	493 ± 25 (5.1)	484 ± 18 (3.7)	477 ± 11 (2.3)
Ethylbenzene	135 ± 7.4 (5.5)	135 ± 7.3 (5.4)	133 ± 7.5 (5.6)	134 ± 7.0 (5.2)
o-Xylene	-	301[b]	119[b]	129[b]
Benzyl chloride	243 ± 12 (4.9)[c]	242 ± 13 (5.3)[c]	244 ± 12 (4.7)[c]	249 ± 14 (5.5)[c]
n-Decane	182 ± 13 (6.9)	183 ± 12 (6.4)	180 ± 10 (5.3)	179 ± 9.4 (5.3)
1,2,3-Trimethylbenzene	1,072 ± 48 (4.4)	1,046 ± 61 (5.8)	1,040 ± 67 (6.4)[c]	1,029 ± 57 (5.6)[c]
o-Cresol	412 ± 17 (4.1)	404 ± 11 (2.0)	399 ± 11 (2.7)	395 ± 9 (2.3)
Nitrobenzene	290 ± 59 (20)	286 ± 62 (22)	272 ± 29 (11)	271 ± 33 (12)

(continued)

Table 55 (Cont'd.)

Compound	Month			
	Jun		Jul	
Methyl chloride	464 ± 2.3 (0.5)	464 ± 2.5 (0.5)	461 ± 8.8 (1.9)	451 ± 20 (4.5)
Propylene oxide	262 ± 7.4 (2.8)	260 ± 7.8 (3.0)	259 ± 7.2 (2.8)	259 ± 7.2 (2.8)
Vinylidene chloride	327 ± 10 (3.2)	329 ± 10 (3.1)	332 ± 8.1 (2.4)	329 ± 15 (4.5)
Allyl chloride	1,167 ± 62 (5.3)	1,134 ± 71 (6.2)	1,096 ± 75 (6.9)	1,039 ± 114 (11)
1,1,1-Trichloroethane	291 ± 38 (13)	280 ± 43 (15)	270 ± 45 (16.6)	270 ± 45 (17)
α-Epichlorohydrin	750[b]	1,012[b]	831[b]	739[b]
Methyl mercaptan	473 ± 7.5 (1.6)	464 ± 16 (3.5)	464 ± 16 (3.5)	452 ± 30 (6.6)
Ethylbenzene	129 ± 6.6 (5.1)	130 ± 6.8 (5.2)	128 ± 6.1 (4.7)	123 ± 9.8 (8.0)
o-Xylene	146[b]	366[b]	309[b]	320[b]
Benzyl chloride	401[b]	601[b]	592[b]	414[b]
n-Decane	178 ± 8.4 (4.7)	180 ± 8.1 (4.5)	175 ± 14 (8.1)	174 ± 16 (9.0)
1,2,3-Trimethylbenzene	1,519[b]	1,407[b]	1,298[b]	2,372[b]
o-Cresol	385 ± 21 (5.6)	376 ± 22 (5.9)	369 ± 23 (6.2)	355 ± 30 (8.4)
Nitrobenzene	567[b]	544[b]	448[b]	265[b]

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[a] Permeation rates are derived from six gravimetric determinations (except for new tubes) and linear regression

[b] analysis - Mean (ng/min) ± S.D. (C.V.).

[c] Not statistically analyzed - new tube or tube with rapidly changing rate.

[d] One of six rates not included in estimation of mean. Excluded rate fails Q test at 90% confidence level. Last three rates statistically analyzed - gradually changing rate.

The permeation rate for chloroprene exhibited a very large coefficient of variation and hence, the studies with this permeation tube are somewhat suspect. However, it was not possible to control the permeation rate because of its high instability and its propensity to polymerize. Gas chromatography/mass spectrometry analysis was performed on Tenax® GC cartridges loaded with "old" and "new" sources of chloroprene in permeation tubes. These results are shown in Figures 53 and 54. The relative proportions of chloroprene to xylenes is higher for the "new" source indicating that the chloroprene in the "old" permeation tube has probably to some extent polymerized.

Nevertheless, the permeation rates for the remaining test compounds were relatively stable.

The permeation rate for bis(2-chloroethyl)ether tube was at one point permeating at an unacceptable rate and therefore a new permeation tube was prepared using appropriate dimensions and materials of construction.

During the period between a pilot study and the storage-stability study, the trimethylbenzene permeation tube developed a severe leak and could not be used. A new permeation tube was prepared.

Calculation of Breakthrough Volumes

Breakthrough volumes were determined for chloroprene, acrylonitrile and furan on the Tenax® GC sampling cartridges. The procedures have been previously described (9). Table 56 lists these breakthrough volumes.

Calibration of Ozone Monitor

On November 6, 1980, a multipoint ozone analyzer calibration was performed by personnel of RTI's Quality Assurance Department. The Bendix Ozone analyzer, model 8002 EPA serial number 100586, was calibrated using the laboratory's stable ozone source (ultraviolet lamp/quartz tube arrangement), ultrapure air (Matheson), and a Dasibi ultraviolet photometer as an assay reference. The calibration was performed in accordance with EPA recommended procedures.

Just prior to the calibration, the Dasibi photometer response was checked in the EQAD/SMD verification laboratory and was found to be in excellent agreement with that of a CSI Photocal 3000 (S/N 10382) ozone generator/photometer that is maintained as an instrument traceable to

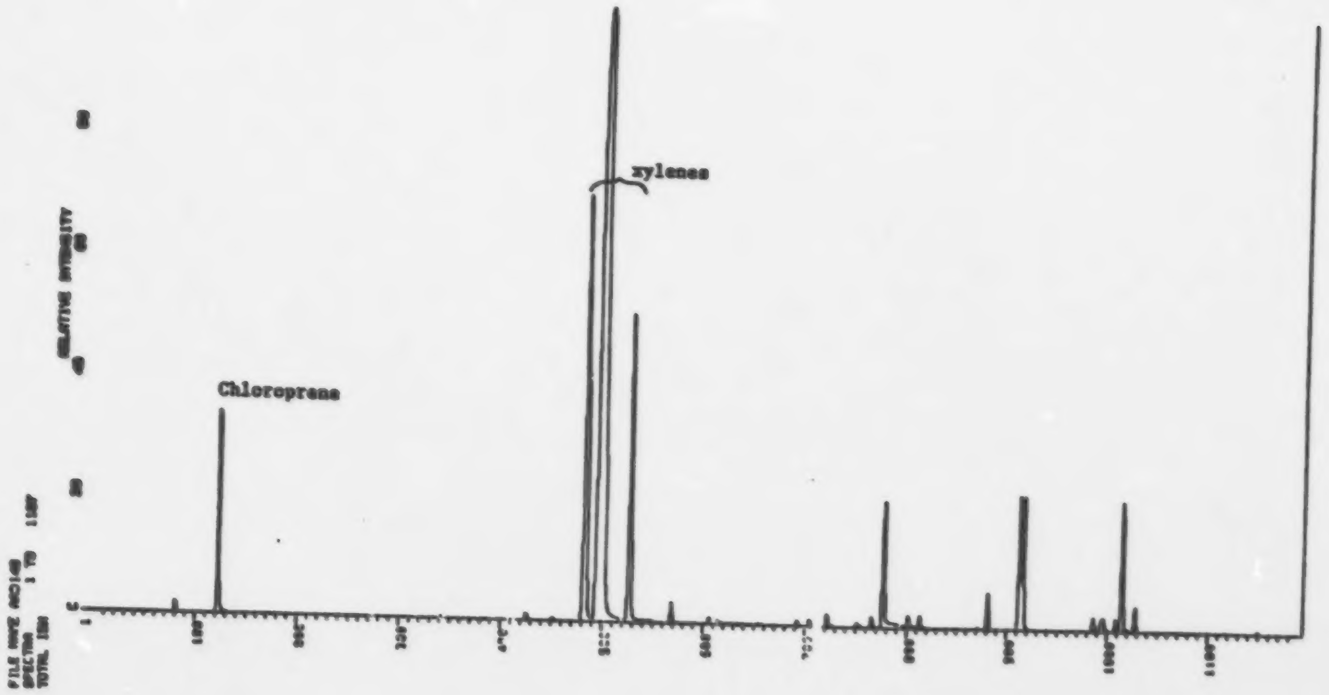


Figure 53. GC/MS/COMP profile of chloroprene in vehicle carrier (xylenes) from permeation tube (old source).

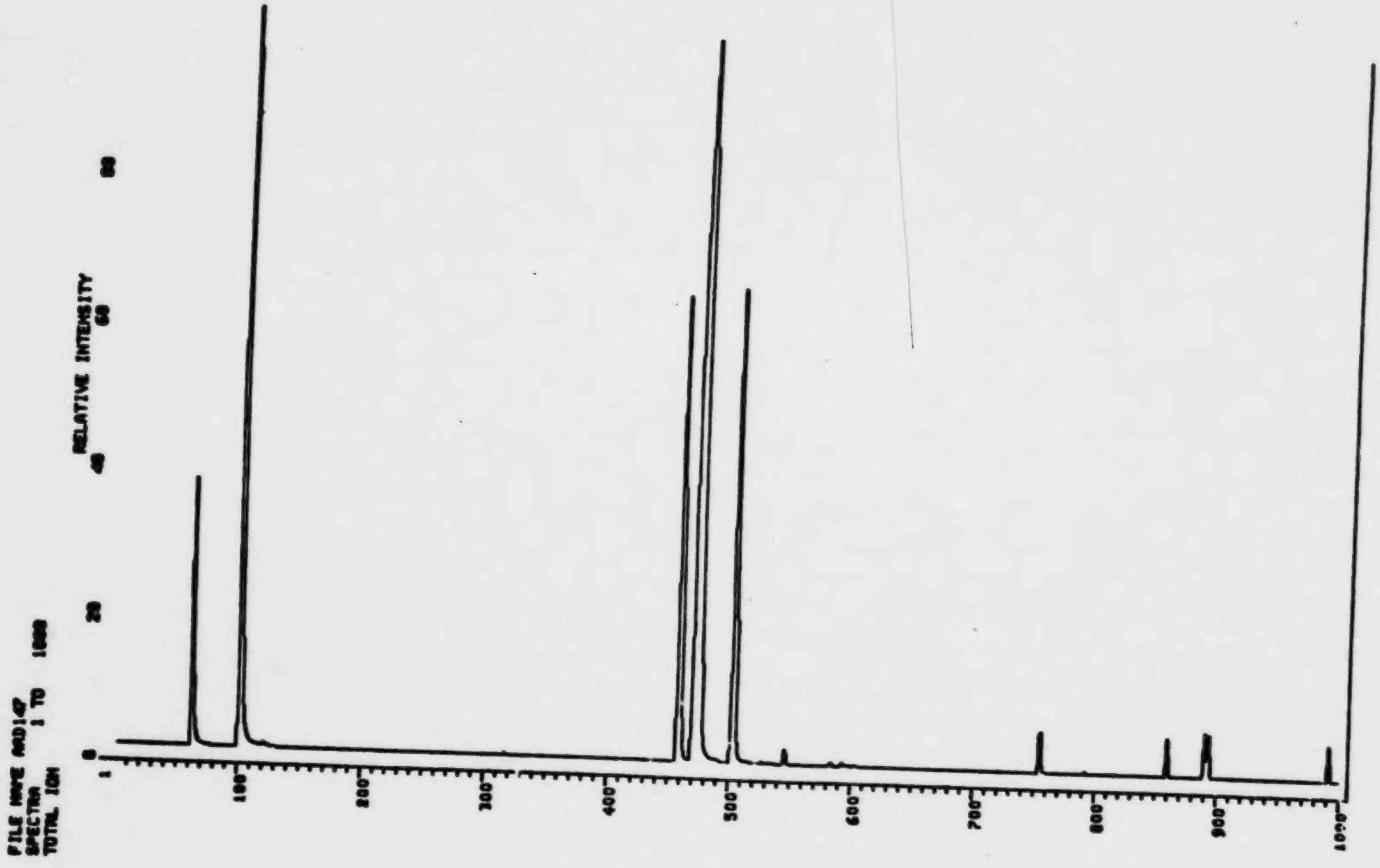


Figure 54. GC/MS/COMP profile of chloroprene in vehicle carrier (xylenes) from permeation tube (new source).

Table 56. BREAKTHROUGH VOLUMES FOR TENAX® GC CARTRIDGE[a]

	Temperature (°F)					
Compound	50	60	70	80	90	100
Chloroprene	34	26	20	15	11	9
Acrylonitrile	11	9	7	5	4	3
Furan	5	4	3	3	2	2

[a] For 1.5 cm i.d. x 6.0 cm Tenax bed, values in liters.

standards in the Quality Assurance Division of EPA's Environmental Monitoring Systems Laboratory.

Results of the precalibration zero and span check and the calibration itself are tabulated in Table 57. The configuration of the equipment at the time of the calibration is illustrated in Figure 55.

The concentrations of ozone as read from the Bendix analyzer agree very well with those read from the photometer; the two readings agree within at least 0.004 ppm over the range considered. Thus, readings made directly from the front panel of the Bendix analyzer are quite acceptable.

Performance Verification of Permeation/Dilution Systems

Calibration of Mass Flow Meters and Controllers--

The flow rates on the portable permeation/dilutor system were checked prior to its use in the studies using an NBS certified bubble flow meter. The flow meters (Tylan) on the system were found to be in error by approximately 15%. The calibration of the flow meters at ambient temperatures was not valid for gases at slightly elevated temperatures. Calibration curves for various settings was made using the bubble flow meter *in lieu* of recalibrating the flow meter readout at the elevated temperatures.

Verification of Dilution Factors--

An experiment was performed to check the dilution factors with the recalibrated system. This consisted of collecting triplicate Tenax cartridges from the manifold after dilutions were made (see Table 58) using two compounds, benzene and tetrachloroethylene. Benzene and tetrachloroethylene were in N_2 (NBS certified tanks).

The flow capability through the permeation system was increased in an attempt to minimize adsorption of polar organic vapors on glass surfaces in the permeation/dilution system. A mass flow controller capable of up to 5 L/min replaced the 2 L/min controller.

A dilution ratio of 1:10 was verified by introducing benzene and tetrachloroethylene from NBS certified cylinders and sampling the effluent (at the manifold) with Tenax® GC cartridges. Table 59 presents the results for undiluted and 1:10 diluted primary standards by the permeation/dilution system.

Table 57. OZONE ANALYZER CALIBRATION RESULTS

Analyzer: Bendix 8002, EPA S/N 100586
Initial Settings: Zero - 015 Span - 554
Final Settings: Zero - 015 Span - 570
Range: 0-0.5 ppm
Time Constant: 10 seconds
Sample and Ethylene Flow: 0.5 COB, Rotameter
Personnel: Sokash, Shores, Demian

Ethylene Pressure: 20 psig
Calibration Photometer: Dasibi Model 1003 AH, S/N 2342
Airmass Flow Controller Settings:
#1: 3.14
#2: zero
#3: 3.98

Ozone Generator Sleeve Setting, cm	Photometer Ozone Concentration[a], ppm	Bendix Ozone Concentration,[b] ppm	Difference Bendix Minus Photometer, ppm	Percent Difference
Precalibration check, prior to span adjustments				
8.0	0.529	0.485	-0.044	-8.3
After span adjustment				
Closed	0.000	0.000	0.000	-
6.0	0.390	0.390	0.000	0.0
5.0	0.313	0.310	-0.003	-0.9
4.0	0.247	0.245	-0.002	-0.8
3.0	0.176	0.172	-0.004	-2.3
2.0	0.105	0.105	0.000	0.0
1.0	0.036	0.040	+0.004	+11.1

[a] As read from digital display of Dasibi photometer, less the zero offset.

[b] As read from front panel meter of Bendix analyzer.

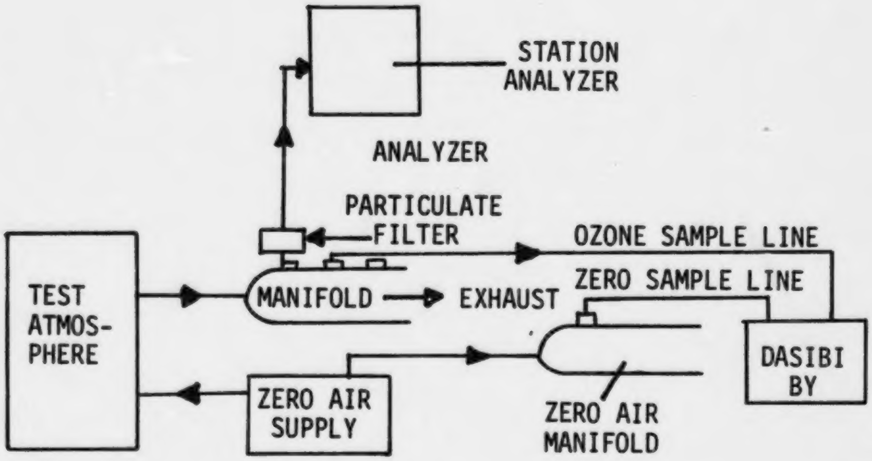

STATION
ANALYZER
ANALYZER
PARTICULATE
FILTER
OZONE SAMPLE LINE
TEST
ATMOS-
PHERE
MANIFOLD
EXHAUST
ZERO SAMPLE LINE
DASIBI
BY
ZERO AIR
SUPPLY
ZERO AIR
MANIFOLD

Figure 55. Schematic configuration used in calibrating the ozone monitor.

Table 58. EXPERIMENTAL PARAMETERS FOR TESTING DILUTION SYSTEM

		Dilution (L/min)					
		Input			Take-out		
Tenax cartridge no.	**Input (L/min)**	**A**[a]	**B**	**C**	**A**	**B**	**C**
1A	1.0	-	-	3.0	-	-	-
1B	1.0	-	-	3.0	-	-	-
1C	1.0	-	-	3.0	-	-	-
2A	1.0	0.9	-	3.0	0.9	-	-
2B	1.0	0.9	-	3.0	0.9	-	-
2C	1.0	0.9	-	3.0	0.9	-	-
3A	1.0	-	0.9	3.0	-	0.9	-
3B	1.0	-	0.9	3.0	-	0.9	-
3C	1.0	-	0.9	3.0	-	0.9	-

[a] Experiment designation.

Table 59. OBSERVED LEVELS FOR BENZENE AND TETRACHLOROETHYLENE FROM DILUTION SYSTEM

Tenax® GC Sample No.	Benzene (ng)	Tetrachloroethylene (ng)
1 (No dilution)	3294	3430
2 (1 → 10 setting)	306	303
3 (1 → 10 setting)	305	281

Verification of GC Calibration Data

Tenax GC Cartridge Analysis--

For calibration of the thermal desorption/GC/chromatography data system, two independent methods were employed. Since the thermal desorption GC/FID system presently cannot be calibrated using liquid injection (solvent would mask the region of interest) it was necessary to verify the calibration utilizing the cartridge technique.

Calibration data were compared from two different methods for loading test compounds on Tenax cartridges. A permeation system, a flash unit, and NBS certified gases were the sources for comparison.

Figure 11 presented the schematic of a vaporization unit for loading organics dissolved in methanol onto Tenax GC cartridges. This system has been previously described (20). Several model compounds were loaded onto Tenax® GC cartridges by using the flash unit to obtain and compare linear regressions (standard curves) with those developed from permeation tubes.

Vapor/nitrogen mixtures in bottled gases at known concentrations were also used to check the calibration curves as part of the quality assurance program.

Two compounds benzene and tetrachloroethylene were available as NBS certified mixtures. These substances were loaded directly onto Tenax® GC cartridges by passing known volumes of vapor-nitrogen through the cartridge. Thus, an implied accuracy was obtained by comparing the three calibration methods.

Calibration curves developed for Group I compounds utilizing permeation tubes were also verified using a flash unit method. Tables 60-62 present these results. Presented are three different masses for which responses were obtained (area as determined by a CDS 111 Varian Chromatography Data System). Linear regressions were determined and correlation coefficients are given (Table 60). The variation of slopes between the permeation system and the flash unit were somewhat larger in the low level calibration than those observed at the high level calibration. This was not unexpected since the trace quantities which were measured were approaching the background levels and quantifiable limits of the technique.

Table 60. GROUP I COMPOUND CALIBRATION DATA USING FLASH UNIT METHOD - HIGH LEVELS

Compound	Mass (ng)	Area ± S.D. (C.V.)	Correlation Coefficient	Slope
Benzene	98	24.18 ± 3.98 (17)	0.99	0.240
	49	11.19 ± 2.60 (23)		
	27	8.78 ± 2.27 (26)		
1,2-Dichloropropane	134	9.44 ± 0.27 (3)	0.99	0.072
	67	4.22 ± 0.28 (7)		
	32	1.64 ± 0.25 (15)		
Toluene	101	22.86 ± 2.65 (12)	0.99	0.230
	50	10.28 ± 3.20 (31)		
	27	5.87 ± 2.18 (37)		
Tetrachloroethylene	185	6.32 ± 0.58 (9)	0.98	0.036
	92	3.44 ± 1.05 (31)		
	45	0.83 ± 0.21 (25)		
Chlorobenzene	128	23.29 ± 0.87 (4)	0.99	0.18
	64	10.04 ± 1.28 (13)		
	31	5.08 ± 0.40 (8)		
1,1,2,2-Tetrachloroethane	166	4.60 ± 0.33 (7)	0.99	0.028
	83	2.62 ± 0.30 (11)		
	43	1.30 ± 0.22 (17)		
Bis-(2-Chloroethyl)ether	137	7.31 ± 0.95 (13)	0.99	0.052
	68	3.36 ± 0.71 (21)		
	33	2.14 ± 0.08 (4)		
m-Dichlorobenzene	146	22.6 ± 1.25 (6)	0.99	0.160
	73	11.85 ± 1.98 (17)		
	35	3.56 ± 0.15 (4)		

Table 61. COMPARISON OF CALIBRATIONS BETWEEN PERMEATION SYSTEM AND FLASH UNIT METHODS - HIGH LEVELS OF GROUP I COMPOUNDS

Compound	Slopes		
	Permeation System	Flash Unit	Δ%[a]
Benzene	0.200	0.240	+20
1,2-Dichloropropane	0.062	0.072	+16
Toluene	0.310	0.230	-26
Tetrachloroethylene	0.037	0.036	-3
Chlorobenzene	0.150	0.180	+20
1,1,2,2-Tetrachloroethane	0.017	0.028	+65
Bis-(2-Chloroethyl)ether	ND[b]	0.052	ND
m-Dichlorobenzene	0.130	0.160	+23

[a] $\Delta\% = \frac{\text{FU Slope} - \text{PS Slope}}{\text{PS Slope}} \times 100\%$

[b] ND = not determined.

Table 62. COMPARISON OF SLOPES FOR STANDARD CURVES BETWEEN PERMEATION TUBE AND FLASH UNIT CALIBRATION METHODS - LOW LEVELS OF GROUP I COMPOUNDS

Compound	Permeation tube calibration	Flash unit calibration	Δ%[a]
1,1,2,2-Tetrachloroethane	0.032	0.024	+25
Chlorobenzene	0.086	0.10	-16
Tetrachloroethylene	0.021	0.024	-14
Toluene	0.13	0.14	-8
Dichloropropane	0.061	0.048	+21
Benzene	0.13	0.14	-8
Bis-(2-chloroethyl)ether	0.00032	0.00034	-6
m-Dichlorobenzene	0.00087	0.00085	+2
Chloroprene	0.18	0.074	+59
Chloroform	0.012	0.015	-25

[a] $\Delta\% = \frac{\text{Perm. Tube - Flash Unit}}{\text{Perm Tube}} \times 100\%$

Sources of synthetic air/vapor mixtures that were commercially available were procured for an independent assessment of the calibration of instrumental systems. Where possible, NBS certified standards were used for cross-checking the calibrations.

Comparison of the slopes of calibration curves generated by three different techniques for benzene and tetrachloroethylene were attempted; however, an interferent prevented a comparison of the NBS Benzene standard with other methods. These results are given in Table 63.

Table 64 gives a comparison of percent recoveries that were calculated for the test compounds from Tenax traps (T_0) using two different calibration techniques. These data give an implied accuracy of the methods since the calibrations employ different approaches.

The final calibration of the instrument was carried out to verify the response of the GC/FID to the Group II compounds. The calibration was carried out using liquid injections of a mixture of most of the Group II compounds in CS_2. The calibration results are given in Table 65. Because of some differences in response between the initial instrument calibration and the final calibration, the latter was used to be applied to data generated in the interference study to compute absolute values. The initial calibration was used for compounds unable to be quantified using the liquid injections.

Calibration data for Group II compounds determined using permeation tubes were compared to calibrations determined using the flash evaporative system. A methanolic solution of the compounds which boil at 60°C or greater was prepared and injected into a hot (250°C) helium stream and the vapors thus generated was loaded onto Tenax cartridges downstream (Fig. 11). Only five determinations for each compound at two spiking levels were used. The results are shown in Table 66. A direct comparison of the two calibrations is shown in Table 67. The correlation coefficient of the calibrations using the flash unit are not as high as might be expected, though this is probably due to the small sample size.

The EPA did not provide to RTI Quality Assurance standards for use in the storage-stability or interference studies involving Group I or Group II compounds.

Table 63. INSTRUMENT CALIBRATION USING DIFFERENT SOURCES OF BENZENE AND TETRACHLOROETHYLENE[a]

Compound	Slope		
	NBS Certified	Flash Unit	Permeation Tube
Benzene	C[a]	0.14[b]	0.13
Tetrachloroethylene	0.022	0.024	0.021

[a] Contamination.

[b] Calibration was for analysis of Tenax® GC cartridges by thermal desorption GC with flame ionization detection.

Table 64. COMPARISON OF PERCENT RECOVERIES FOR TEST COMPOUNDS FROM TENAX® GC TRAPS USING TWO DIFFERENT CALIBRATION TECHNIQUES

Compound	Flash unit (T_0 = 0 da)	Permeation (T_0 = 0 da)	Δ%[b]
Chloroform	111 ± 19 (17)[a]	111 ± 21 (19)	0
Benzene	59 ± 8 (13)	65 ± 9 (14)	+9.2
1,2-Dichloropropane	126 ± 17 (14)	101 ± 14 (14)	-25
Toluene	88 ± 9 (11)	91 ± 10 (11)	+3.3
Tetrachloroethylene	85 ± 6 (7)	97 ± 7 (7)	+12
Chlorobenzene	90 ± 6 (6)	105 ± 7 (7)	-14
1,1,2,2-Tetrachloroethane	122 ± 5 (4)	93 ± 4 (4)	-31
Bis-(2-chloroethyl)ether	102 ± 5 (5)	106 ± 5 (5)	+4
m-Dichlorobenzene	137 ± 6 (4)	103 ± 6 (4)	+33

[a] Mean percent recovery, ± S.D. (C.V.).

[b] $\Delta T = \frac{\text{Permeation Tube Calibration - Flask Unit Calibration}}{\text{Permeation Tube Calibration}} \times 100\%$

Table 65. CALIBRATION DATA FROM LIQUID INJECTION OF GROUP II COMPOUNDS

Compound	Mass (ng)	Area Mean ± S.D. (C.V.)	Slope	Correlation Coefficient
Propylene oxide		solvent interference		
Vinylidene chloride		solvent interference		
Allyl chloride		solvent interference		
1,1,1-Trichloroethane	1,339	241 ± 49 (20)	0.156	0.994
	6,695	1,143 ± 96 (8)		
	10,042	1,586 ± 7.5 (0.5)		
α-Epichlorohydrin	1,180	329 ± 98 (30)	0.238	0.998
	5,900	1,457 ± 34 (2)		
	8,850	2,153 ± 27 (1.2)		
Ethylbenzene	867	757 ± 5.2 (0.7)	0.844	0.984
	4,335	4,038 ± 646 (16)		
	6,502	5,455 ± 62 (1.1)		
o-Xylene	880	786 ± 44 (6)	0.880	0.985
	4,400	4,233 ± 681 (16)		
	6,600	5,763 ± 44 (0.8)		
Benzyl chloride	1,100	630 ± 36 (6)	0.625	0.992
	5,500	3,381 ± 298 (9)		
	8,250	3,709 ± 441 (12)[a]		
n-Decane	730	619 ± 26 (4)	1.244	0.985
	3,650	3,817 ± 585 (15)		
	5,475	6,597 ± 498 (8)		

(continued)

Table 65 (Cont'd.)

Compound	Mass (ng)	Area Mean ± S.D. (C.V.)	Slope	Correlation Coefficient
1,2,3-Trimethylbenzene	894	697 ± 41 (6)	0.679	0.989
	4,450	3,343 ± 379 (11)		
	6,675	4,581 ± 210 (5)		
o-Cresol	1,027	657 ± 50 (8)	0.656	0.996
	5,140	3,490 ± 314 (9)		
	7,710	5,017 ± 70 (1.4)		
Nitrobenzene	1,204	644 ± 79 (12)	0.380	0.990
	6,020	2,601 ± 342 (13)		
	9,030	3,595 ± 27 (0.7)		

[a] High level calibration point was not used to obtain slope and correlation coefficient.

Table 66. INSTRUMENT CALIBRATION USING FLASH UNIT METHOD

Compound	Mass (ng) Low Level	Mass (ng) High Level	Slope	Correlation Coefficient
1,1,1-Trichloroethane	1,340	3,350	0.179	0.742
α-Epichlorohydrin	1,180	2,950	0.274	0.812
Ethylbenzene	870	2,170	0.855	0.831
_o_-Xylene	880	2,200	0.907	0.833
Benzyl chloride	1,100	2,750	0.267	0.747
_n_-Decane	750	1,825	0.858	0.824
1,2,3-Trimethylbenzene	890	2,240	0.747	0.892
_o_-Cresol	1,030	2,570	0.391	0.883
Nitrobenzene	1,200	3,010	0.587	0.873

Table 67. COMPARISON OF SLOPES FOR STANDARD CURVES BETWEEN PERMEATION TUBE AND FLASH UNIT CALIBRATION METHODS - TENTATIVE RESULTS

Compound	Permeation Tube Calibration	Flash Unit Calibration	Δ%[a]
1,1,1-Trichloroethane	0.424	0.179	+58
α-Epichlorohydrin	0.381	0.274	-28
Ethylbenzene	1.015	0.855	-16
o-Xylene	1.236	0.907	+27
Benzyl chloride	0.236[b]	0.267	-13
n-Decane	0.966	0.858	+11
1,2,3-Trimethylbenzene	0.788	0.747	+5.2
o-Cresol	0.258[b]	0.319	-24
Nitrobenzene	1.959	0.587	+70

[a] $\Delta\% = \frac{\text{Perm. Tube - Flash Unit}}{\text{Perm. Tube}} \times 100\%$

[b] Tentative value.

Quality Control of GC Calibration Data; Containers--

The calibration gases were taken directly from the permeation/dilution system into the gas chromatographic system described earlier. The sample transfer line was heated and also was flushed with sample three times before the sample was collected in the GC-cryogenic trap for measurement. This flushing consisted of drawing sample from the permeation/dilution system by vacuum (GC sample loading system). Until the GC system was pressurized to one atmosphere (the GC cryogenic trap was by-passed during flushing). The GC system calibration was not verified using other gaseous standards. This is not considered a major problem as calibration was based on direct use of permeation tubes which are considered as reliable as diluting a standard gas (in a cylinder) from the ppm to the ppb level.

Blanks and Controls

Traps--

Storage and Stability Studies--Prior to initiating the collection and storage study, Tenax® GC, charcoal and nickel cryogenic traps were examined for background interference. Blanks were collected in triplicate from the permeation/dilution system (no test compounds) for analysis at t_0, t_3, and t_7 during the storage study. This was to pinpoint any background interference or false positive measurement that occurred during the analysis of samples.

Interference Studies--Sampling traps were also examined for cleanliness prior to initiating this study. Blanks were taken of the permeation/dilution system to determine the extent of background before proceeding with test compounds and the introduction of inorganic gases. Control samples using Tenax® GC, charcoal and cryogenic traps were taken (sampling of air-vapor mixture without presence of inorganic gases) for making a comparative analysis. In addition, a glass fiber filter [impregnated with and without sodium thiosulfate (1-5 mg)] was used prior to the Tenax® GC cartridges.

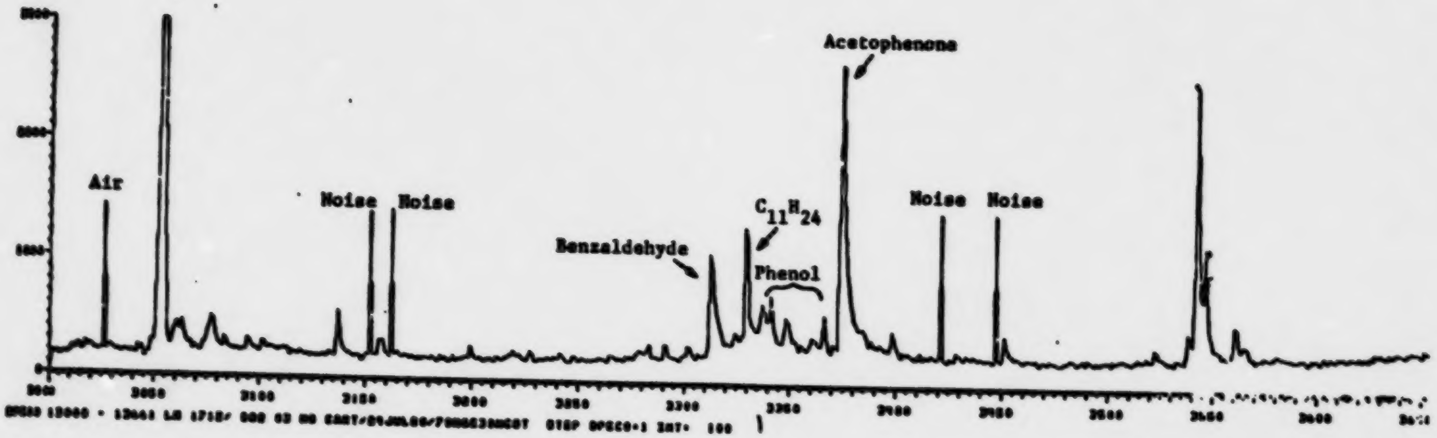
All samples taken from the portable permeation system with the inorganic gases present were collected in triplicate with and without a glass fiber filter impregnated with 10% sodium thiosulfate in line between the manifold and Tenax GC cartridges. This experimental design differentiated between photochemical reactions occurring within the dilution bulb themselves and reactions on Tenax® GC. Comparison of the chromatograms with and without the filters showed a disappearance of the major peaks previously reported - phenol, acetophenone, benzaldehyde (Fig. 56) - when glass fiber filters with sodium thiosulfate were utilized. These results suggested that these compounds were products of a reaction between the inorganic gases (probably ozone) and Tenax® GC itself.

During the interference experiments, solvent desorbed charcoal produced two contaminants during analysis by GC/ECD. This background was not present during the storage-stability studies. The two background constituents were present in all of the charcoal tubes tested for background (i.e. unexposed tubes). Subsequently a new lot of NIOSH charcoal tubes was purchased from Applied Science (Bellfonte, PA). Several of the new charcoal tubes were solvent desorbed (methanol/carbon disulfide) and chromatographed using the standard conditions for analysis of test model compounds. The identical background was still present (Fig. 57). New sources of redistilled methanol and carbon disulfide were obtained; however, the solvents used were clean when examined by GC/ECD. Subsequently, the background components were examined by GC/MS.

An extract of an unexposed charcoal tube was analyzed by GC/MS. These results are given in Fig. 58 and 59. The first component was tentatively identified as 2-ethylhexanol. The second appears to have an empirical formula of $C_4H_{10}S_2$. The $C_4H_{10}S_2$ contaminant interfers with measurement of bis(2-chloroethyl)ether while 2-ethylhexanol coelutes with 1,1,2,2-tetrachloroethane. The magnitude of 2-ethylhexanol, however, is small relative to the 1,1,2,2-tetrachloroethane response in the high and low level studies.

Cannisters--

Storage and Stability Studies--Bags, glass bulbs and steel containers were checked for cleanliness after cleaning. This check consisted of filling the containers with clean air and then analyzing this air as soon as possible using the GC system described previously. The bags were cleaned and tested immediately before use in the recovery studies. The containers were considered clean if background peaks at retention times equivalent to those of test compounds were essentially equivalent to those found with laboratory-supplied, dry, clean air analyzed directly.



Reproduced from
best available copy.

Figure 56. GC/MS/COMP profile of background for 30 L air sample from permeation/dilution systems with 340 ppb O_3, 320 ppb NO_x, 200 ppb SO_2, and 90% humidity present. Major sources of hydrocarbons traced to NO supply.

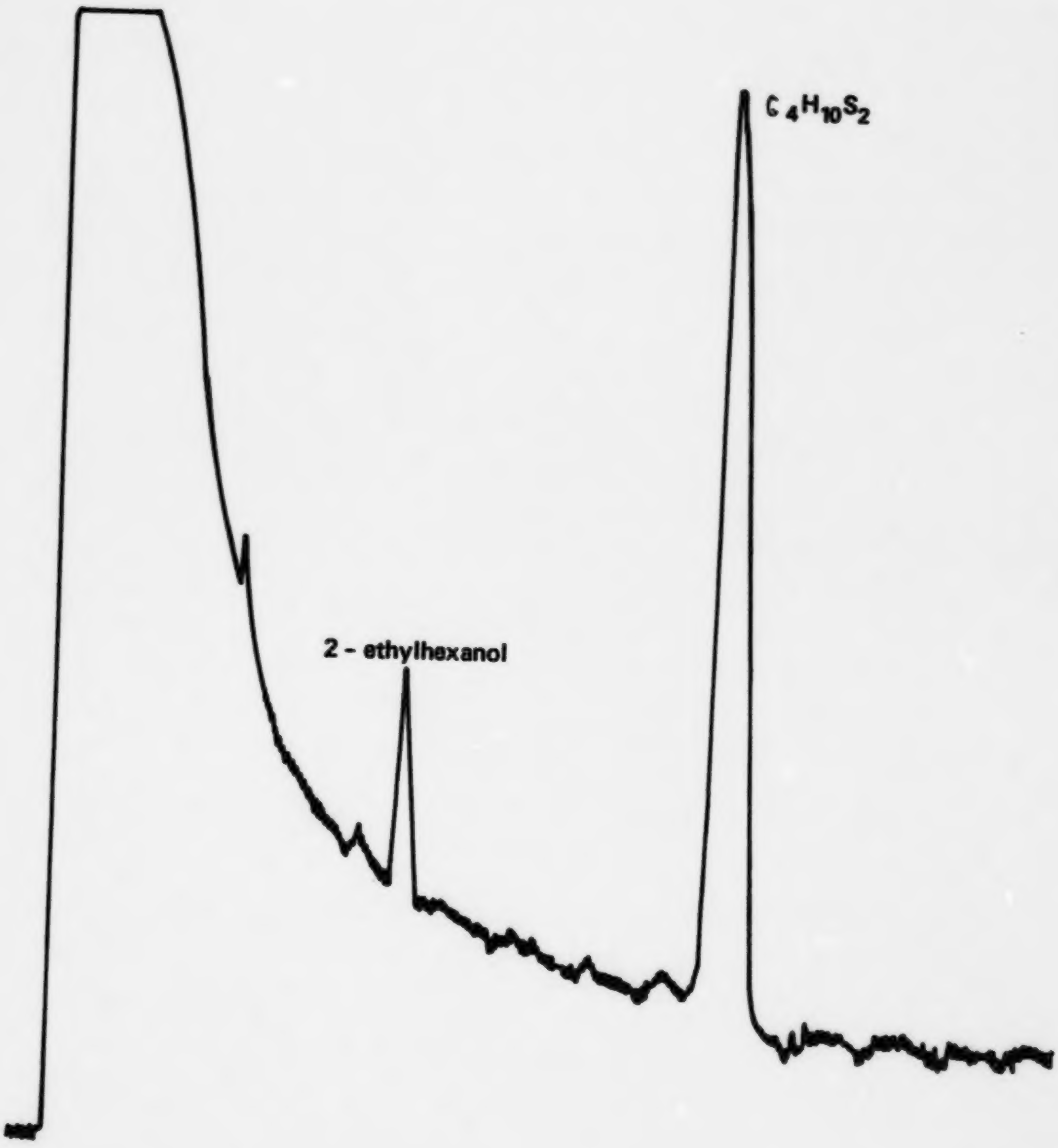
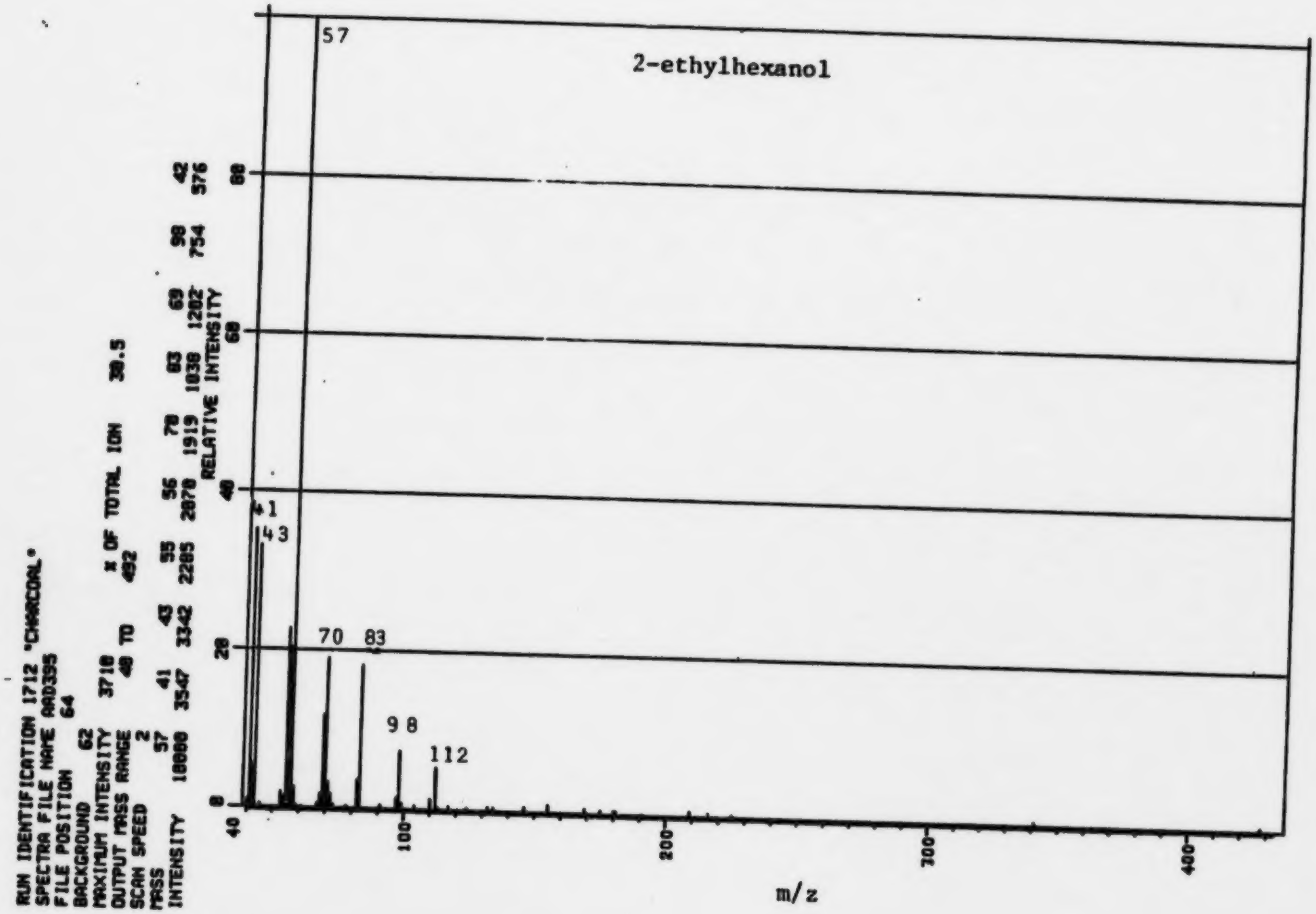


Figure 57. Chromatogram depicting background for solvent desorbed unexposed NIOSH charcoal tubes.



```
RUN IDENTIFICATION 1712 "CHARCOAL"
SPECTRA FILE NAME AAD395
FILE POSITION      64
BACKGROUND      62
MAXIMUM INTENSITY      3710      % OF TOTAL ION      30.5
OUTPUT MASS RANGE      40 TO      492
SCAN SPEED      2
MASS            57      41      43      55      56      70      83      69      98      42
INTENSITY    10000    3547    3342    2285    2070    1919    1838    1202     754     576
```

Figure 58. Mass spectrum of background contaminant from charcoal tube.

```
RUN IDENTIFICATION 1712 "CHARCOAL"
SPECTRA FILE NAME AAD395
FILE POSITION     67
BACKGROUND      65
MAXIMUM INTENSITY   8140        % OF TOTAL ION    24.3
OUTPUT MASS RANGE     40 TO    492
SCAN SPEED        2
MASS            122    75    47    45    46    91    77   124    61    76
INTENSITY     10000  8719  5815  2766  2428  1941  1216  1083   885   883
```

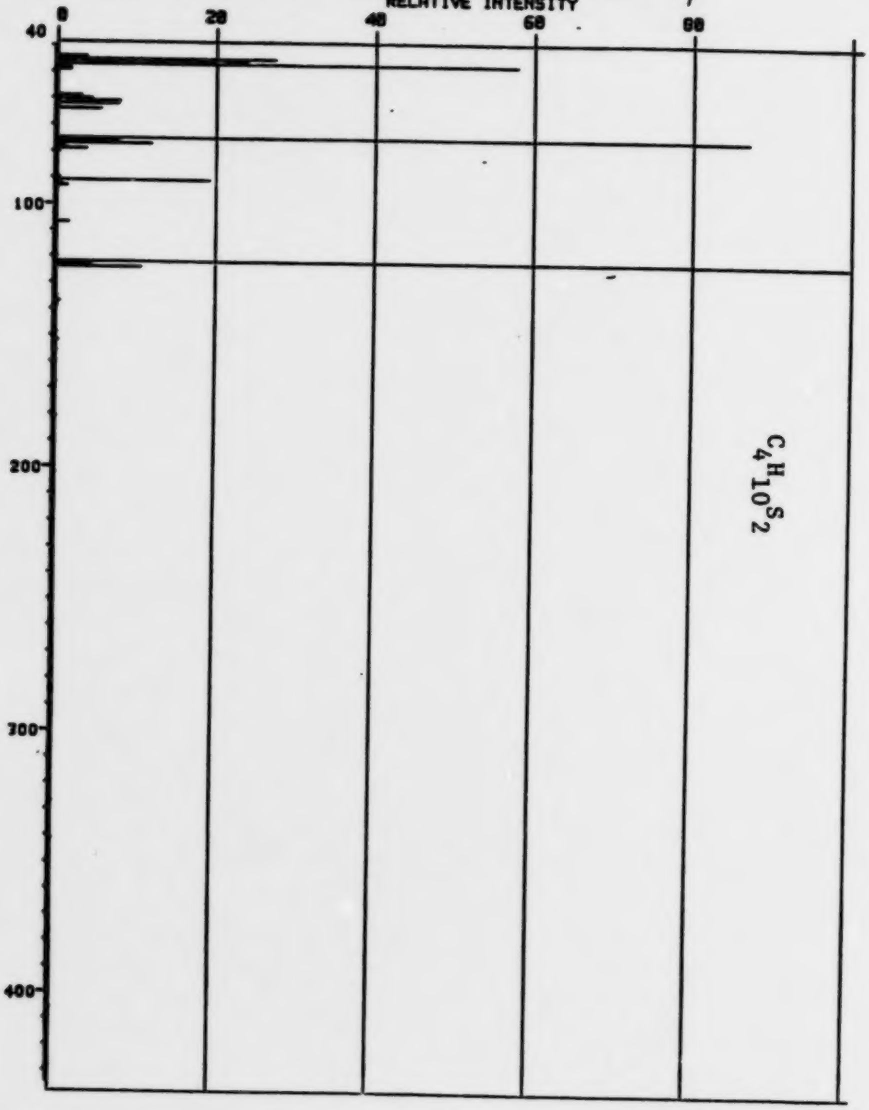


Figure 59. Mass spectrum of background contaminant from charcoal tube.

Blank samples for each container type were loaded when the test compounds were loaded. A typical analysis set was three containers of one type containing test compounds and one container of that type containing clean air. More control samples for each type of container were not prepared and analyzed as each sample required typically 1 1/2 hours for analysis. Background peak areas found in the control samples for each container type on Days 0, 3 and 7 were subtracted from the areas determined for the test compounds on Days 0, 3 and 7 respectively.

Interference Studies--The model compound conentrations were generated with the portable permeation/dilution system which has been described in earlier reports. The organic vapor concentrations were all less than 100 ppb. Interference gases were generated at two different levels. The high level concentrations were 360 ppb ozone, 360 ppb nitrogen dioxide, 200 ppb sulfur dioxide, and 90% relative humidity at 20°C. The low level interference concentrations were 75 ppb ozone, 100 ppb nitrogen dioxide, 10 ppb sulfur dioxide, and 26% relative humidity at 20°C. Clean air was humidified by passing it thorugh a fritted bubbler containing water and then irradiated with ultraviolet light to generate ozone. The ozone/water vapor in air mixture was mixed with nitric oxide and sulfur dioxide from certified gas cylinders to generate the required concentrations of each component. The entire interferent gas mixture was mixed with the model compounds in the clean air stream within a mixing bulb contained in the permeation/dilution system oven which was heated to approximately 200°C.

The relative humidity was monitored with a YSI Dew Point Sensor. Ozone and nitrogen dioxide concentrations were monitored with a Bendix ozone monitor. Ozone concentrations were measured directly whereas nitrogen dioxide concentrations were measured by the difference in ozone concentration after gas phase titration. Sulfur dioxide concentrations were not monitored.

Chronology of Quality Control Practices

Steps taken to provide quality control and assurance of the data generated was discussed above. Table 68 presents a summary chronological record of QA/QC procedures performed during the storage-stability and interference studies.

Table 68. CHRONOLOGICAL RECORD OF QUALITY CONTROL AND QUALITY ASSURANCE PROCEDURES PERFORMED DURING STORAGE-STABILITY AND INTERFERENCE STUDIES

Experiment	Dates	Quality Control and Assurance Performed
Storage-Stability (High Level) (Group I Compounds) (Sorbents and Traps)	1/25/80	· Calibration of TD/HRGC System (Varian Model 3700, CDS-111 Chromatography Data System)
	2/5/80	· Calibration of GC/FID (Fisher Victoreen Model 4400)
	2/20/80	· Recalibration/Verification of TD/HRGC System
	3/30/80	· Verification of Flow Meters and Controllers on Permeation/ Dilution System
	3/31/80	· High Level Storage-Stability Study Initiated[a]
	4/16/80	· Calibration of GC/ECD (Fisher Victoreen)
	4/22/80	· Verification of TD/HRGC Calibration Using Independent Method (Flash Unit)
	4/25/80	· Verification of TD/HRGC Calibration Using Independent Method (NBS certified gases)
Storage-Stability (Low Level) (Group I Compounds) (Sorbents and Traps)	5/8/80	· Low Level Storage-Stability Study Initiated[a]
	5/12/80	· Breakthrough Volumes for Chloroprene, Furan and Acrylonitrile Determined for Tenax GC Cartridge
	5/20/80	· Verification of Flow Meter Calibrations for Permeation/ Dilutor System
	6/18/80	· Low Level Storage-Stability Study Continued[a]

(continued)

Table 68 (cont'd.)

Experiment	Dates	Quality Control and Assurance Performed
	7/2/80	• Verification of TD/HRGC Calibration Using Independent Method (Flash Unit)
	7/7/80	• Verification of TD/HRGC Calibration Using Independent Method (NBS certified gases)
	7/11/80	• Analysis of Chloroprene/Xylene Mixture (of Permeation Tube) by GC/MS to Verify Chloroprene Concentration
Interference Study (High Level) (Group I Compounds) (Sorbents and Traps)	8/6/80	• Calibration of NO_x Monitor
	8/6/80	• Calibration of O_3 Monitor
	8/6/80	• Verification of Flow Meter Calibrations for Permeation/ Dilution System
	8/11/80	• Interference Study Inititated (Tenax GC Traps)[a]
	8/11/80	• Identification of Background on Exposed Tenax GC and Unexposed Charcoal Traps by GC/MS
	9/6/80	• Verification of NO_x Monitor Calibration
	9/6/80	• Verification of O_3 Monitor Calibration
	9/6/80	• Verification of Flows on Permeation/Dilution System
	9/12/80	• Interference Study Continued (Charcoal and Cryogenic Traps)[a]
	9/12/80	• Calibration of GC/ECD
Interference Study (Low Level) (Group I Compounds) (Sorbents and Traps)	9/22/80	• Calibration of NO_x Monitor
	9/22/80	• Calibration of O_3 Monitor

(continued)

Table 68 (cont'd.)

Experiment	Dates	Quality Control and Assurance Performed
	9/25/80	· Interference Study Initiated (Tenax® GC and Charcoal Traps)[a]
	10/6/80	· Verification of NO_x Monitor Calibration
	10/6/80	· Verification of O_3 Monitor Calibration
	10/6/80	· Verification of Flows on Permeation/Dilution System
	10/8/80	· Interference Study Continued (Cryogenic Traps)[a]
	10/16/80	· Verification of TD/HRGC Calibrations
	10/16/80	· Verification of GC/ECD Calibrations
	11/6/80	· Audit of NO_x and O_3 Monitor Calibrations
Storage-Stability (High Level) (Group II Compouds) (Sorbents and Traps)	5/19/81	· Calibration of Thermal Desorption - High Resolution GC/FID System for Tenax GC Cartridge Analysis
	5/27/81	· Recalibration of TD/HRGC System
	6/2/81	· Purity Check of Propylene Oxide
	6/4/81	· Verification of Calibration of TD/HRGC System (Flash Loading Technique)
	6/5/81	· Calibration of Nutech Sampling Pumps
	6/8/81	· Storage Study on Group II Compounds
	6/24/81	· Calibration of TD/HRGC System for Methyl Chloride and Methyl mercaptan

(continued)

Table 68 (cont'd.)

Experiment	Dates	Quality Control and Assurance Performed
Interference Study (High and Low Level) (Group II Compounds) (Sorbents and Traps)	7/3/81	· Background Check of Permeation/Dilution System
	7/15/81	· High Level Interference Study
	7/17/81	· Low Level Interference Study
	8/3/81	· Calibration Check of Group II Compounds on TD/HRGC System
	8/25/81	· Calibration Verification for TD/HRGC System by Injection of Liquid Standards
	8/26/81	· Calibration Check for TD/HRGC System
Storage-Stability (High Level) (Group I Compounds) (Containers)	4/28/80	· Initial Calibration of GC/FID (Perkin Elmer 3920)
	5/27/80	· Improved temperature control of permeation/dilution system.
	5/28/80	· Permeation system flow controls evaluated and calibrated.
	10/15/80	· Checked and recalibrated permeation/dilution system flow controls.
	12/3/80	· Tested new SCOT SE-30 column in order to improve resolution.
	1/2/81	· House clean air generation system replaced in order to improve moisture removal and increase output pressure.
	1/6/81	· Storage stability study initiated[a].
	1/8/81	· Checked permeation/dilution system flows.
	2/4/81	· Recalibration of GC/FID

(continued)

Table 68 (cont'd.)

Experiment	Dates	Quality Control and Assurance Performed
Storage-Stability (Low-Level) (Group I Compounds) (Containers)	6/12/80	· Containers cleaned
	6/18/80	· Calibration of GC/FID (Perkin Elmer 3920)
	6/23/80	· Recalibration of GC/FID. Low level study discontinued because of inadequate detection limit with volume of sample taken from container.
Interference Study (High Level) (Group I Compounds) (Containers)	7/30/81	· Initiated measurements with low-level interferents.
	7/28/81	· Initiated measurements with high-level interferents.
	8/4/81	· Calibration of GC/FID.
Storage-Stability (High Level) (Group II Compounds) (Containers)	6/19/81	· Calibration of GC/FID.
	6/24/81	· Calibration check
	6/26/81	· Calibration check
	6/8/81	· Initiated storage-stability study.
	7/1/81	· Calibration check.
	7/8/81	· Calibration check.
Interference Study (High Level) (Group II Compounds) (Containers)	7/15/81	· Initiated measurements with high-level interferents.
	7/17/81	· Initiated measurements with low-level interferents.
	7/14/81	· Calibration check (extension of calibration check from Group II storage-stability study).

(continued)

Table 68 (cont'd.)

Experiment	Dates	Quality Control and Assurance Performed
Bag Contamination Study	7/28/80	• Initiated study of sources of bag contamination
	7/28/80	• Bags leak-tested
	7/29/80-8/9/80	• Bag loading, storage and analysis experiments
	9/9/80-9/23/80	• Repeated bag loading; storage and analysis experiments
	9/29/80	• Initiated evaluated of bag cleaning methods
	11/3/80	• Continued bag loading, storage and analysis experiments

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[a] With the initiation and continuation of each set of experiments "background" controls were taken of the permeation/dilution system in addition to the normal trap blanks.

SECTION 8

DESIGN AND FABRICATION OF AN AUTOMATIC SAMPLER

DESIGN FEATURES

Efforts were made to design a sampler that would be reasonably inexpensive but which adequately satisfied the most important requirements of collecting air samples on sorbent cartridges. A summary of the design features are as follows:

(1) The design of the sampling heads was to accommodate 12 samples with six in each sampling head and with provisions for one blank in the center position.

(2) A sampling head with bolt-on cap to be quickly accessible.

(3) Sample head mounting in a down position with a cover and slipjoint hinge.

(4) Twelve 1/8 inch lines to the console approximately 10 feet long.

(5) Provisions for shipping cartridges in sampler head.

(6) Electrical and mechanical switching and flow control on front panel of console.

(7) Variable orifices for low flow rate settings and range.

(8) Manual flow adjustment of each channel through variable orifices (valve).

(9) A mass flow meter which is switchable to each channel with the ability to obtain total flow.

(10) The capability to check the mass flow meter or calibrate.

(11) Solid-state times preferred over electromechanical with also provisions for a clock integrator, printer, and manual mode.

(12) Seventy-two hour maximum sample time for six samples; 24 hours maximum single sample with provisions also for automatic or manual setting available for any time period.

(13) Reset capability for flow integrator after each sample but not after power failure.

(14) Options on the console for series (1-12) samples and duplicate parallel sampling.

(15) Sampling rates settable from 7 mL/min to 1.5 L/min.

(16) The automatic sampler was to operate on alternating current.

MECHANICAL DESIGN

Figure 60 depicts a schematic of the automatic sampler and its specifications are given in Table 69. It consists of two sampling heads which allows for duplicate sampling. Each sampling head housing six sampling cartridges plus one blank. Figure 61 depicts the control panel for the automatic sampler and Table 70 lists the control settings. The major components shown are a flow meter (the flow may be monitored through either sampling head independently or in combination), and a printer (records the total volume of air sample/unit of time). The sampling periods available are of 15, 30, 45 and 60 min and 1/2, 2, 3, 6, 8 and 12 hr. Duplicate or single cartridge sampling is possible (in a serial fashion for collection of up to 12 sampling cartridges) for a maximum of 12 hrs/sampling cartridge. Flow control for each sampling head is achieved with a variable orifice.

Figures 62 and 63 depict the flow measurement processes and the console flow diagram for the automatic sampler.

Figures 64-66 depict the schematic of a sample cartridge collector. The cartridge collector is constructed of aluminum with accommodation of up to 7 cartridges (Fig. 67), of which 6 would be used for sampling and the 7th a blank. Figure 68 gives the sample holder set in a sample cover. Figure 69 depicts the heated sample cover for the sample cartridge collector.

FLOW DIAGRAM AND ELECTRONIC CONTROLS

The overall flow diagram was shown in Figure 63. An expanded view of the manifold is given in Figure 70 and of the muffler in Figure 71.

The control and timing functions of the sampler are shown in the electronic schematic (Figs. 72 and 73). The timing circuit generates a series of pulses at a frequency of 100 KHz (Fig. 73). This frequency is reduced by means of divide counters to the desired sampling frequency, i.e., 15 minutes to 24 hours. The time cycle switches on the front panel pack up the time

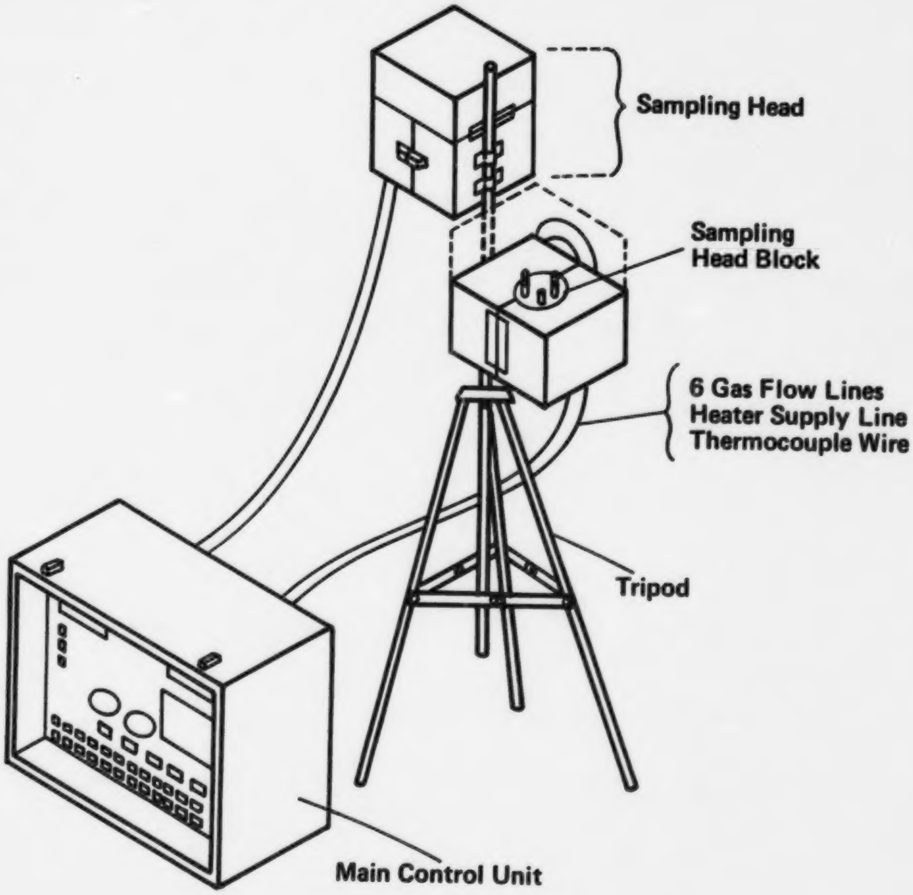

Sampling Head
Sampling Head Block
6 Gas Flow Lines
Heater Supply Line
Thermocouple Wire
Tripod
Main Control Unit

Figure 60. Automatic sampler.

Table 69. SPECIFICATIONS OF THE AUTOMATIC AIR SAMPLER

Item	Specification
Input voltage	120 volts AC, grounded
Fuse	3 amp, 250 volt
Flowmeter (Model AFSC 500):	
minimum flow rate	0 sccm
maximum flow rate	500 sccm
accuracy	±1% @ maximum flow rate
operating temperatures	0-40°C
response time	25 secs to 90% of reading
Flow integrator	
minimum volume	0.01 liters
maximum volume	9999 liters
Maximum number of samples	12
Maximum number of controls	2
Total number of cartridges	14
Sampling Periods	15, 30, and 45 min; 1, 1.5, 2, 3, 4, 6, 8, 12, and 24 hrs
Number of sampling periods per sampling sequence	6 (parallel mode); 12 (serial mode)
Printer paper	electrosensitive (100 ft rolls) United Systems Corp. P/N 19-17210, or Radio Shack P/N 26-1412

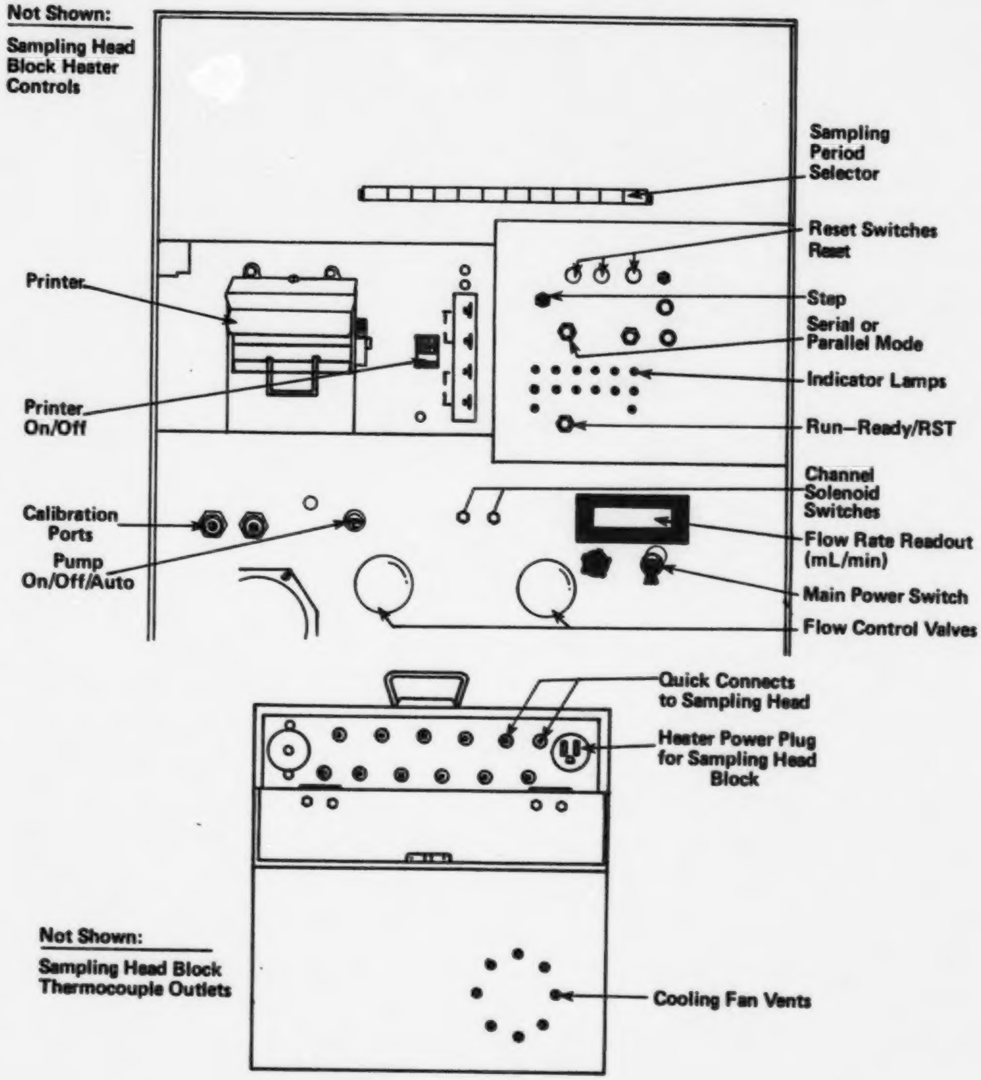

Not Shown:
Sampling Head Block Heater Controls
Sampling Period Selector
Reset Switches
Reset
Printer
Step
Serial or Parallel Mode
Indicator Lamps
Printer On/Off
Run–Ready/RST
Channel Solenoid Switches
Calibration Ports
Flow Rate Readout (mL/min)
Pump On/Off/Auto
Main Power Switch
Flow Control Valves
Quick Connects to Sampling Head
Heater Power Plug for Sampling Head Block
Not Shown:
Sampling Head Block Thermocouple Outlets
Cooling Fan Vents

Figure 61. Main control unit.

Table 70. SWITCH POSITIONS AND CONTROL SETTINGS AT POWER UP OF AUTOMATIC SAMPLER

Switch or Control	Position or Setting
Sampling Period Selector	Any
Printer On/Off	Off
Head Heater Controls	Lowest Setting (full CCW)
Serial/Parallel Switch	Any
9 Sec/Prog. Switch	Non-functional
Run/Ready-Reset Switch	Run
Pump	Off
Channel Solenoid Switches	Up
Flow Control Valves	Any Setting

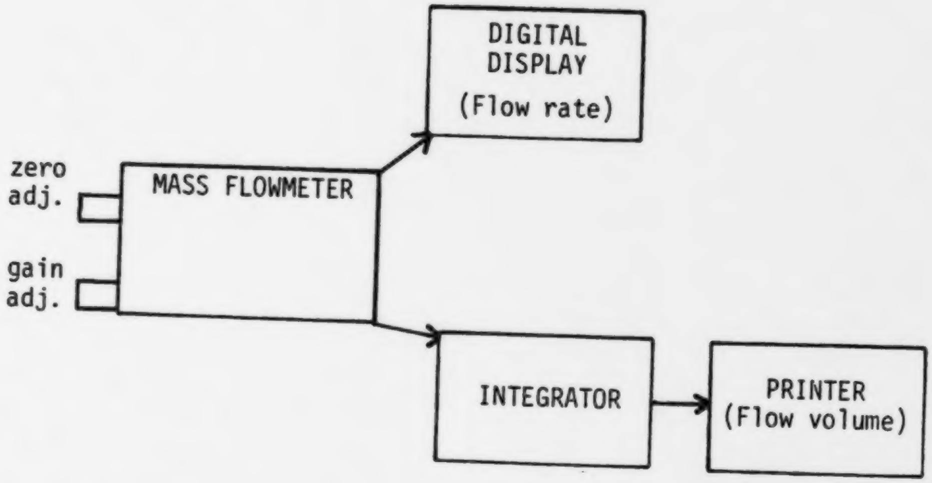

DIGITAL DISPLAY
(Flow rate)
zero adj.
MASS FLOWMETER
gain adj.
INTEGRATOR
PRINTER
(Flow volume)

Figure 62. Functional diagram of flow measurement processes.

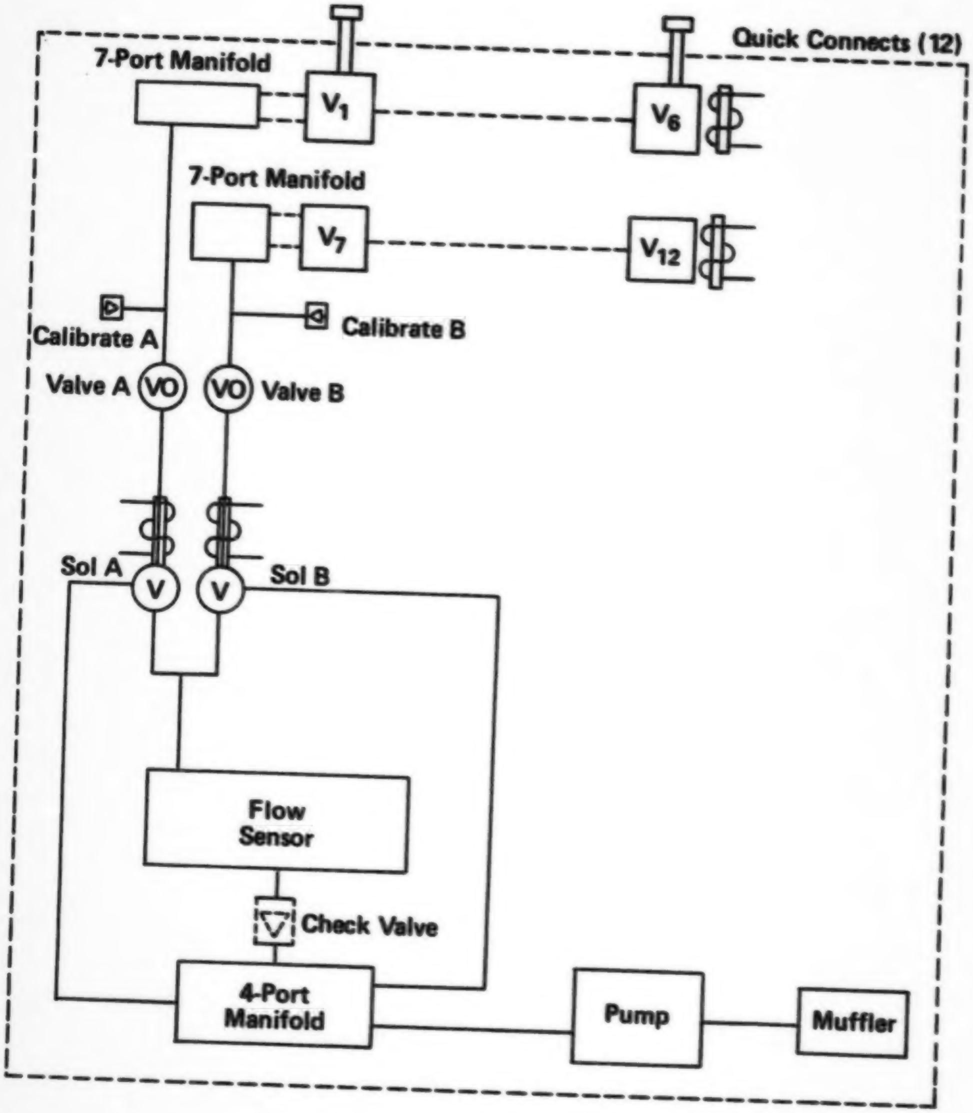

Quick Connects (12)
7-Port Manifold
V1
V6
7-Port Manifold
V7
V12
Calibrate A
Calibrate B
Valve A
VO
VO
Valve B
Sol A
V
V
Sol B
Flow Sensor
Check Valve
4-Port Manifold
Pump
Muffler

Figure 63. Flow schematic of the main control unit.

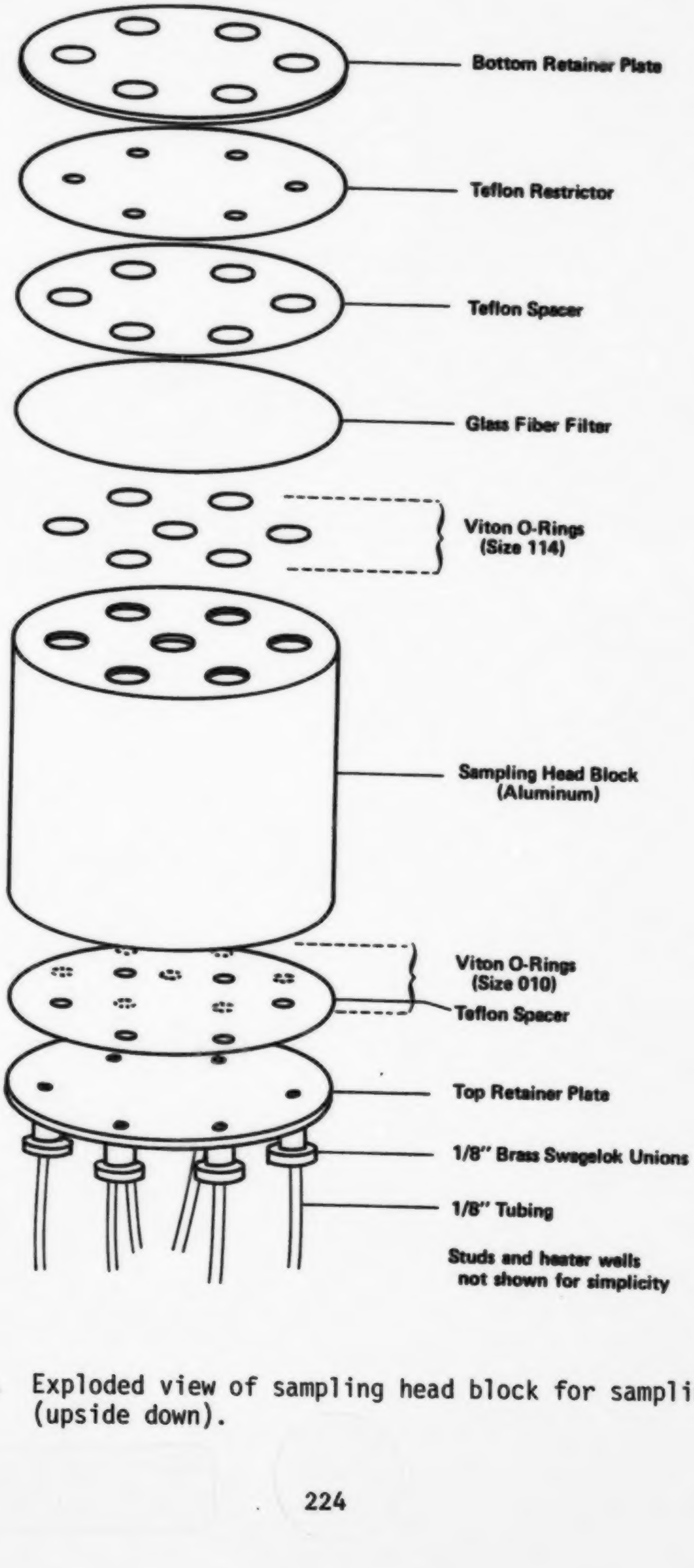

Bottom Retainer Plate
Teflon Restrictor
Teflon Spacer
Glass Fiber Filter
Viton O-Rings (Size 114)
Sampling Head Block (Aluminum)
Viton O-Rings (Size 010)
Teflon Spacer
Top Retainer Plate
1/8" Brass Swagelok Unions
1/8" Tubing
Studs and heater wells not shown for simplicity

Figure 64. Exploded view of sampling head block for sampling mode (upside down).

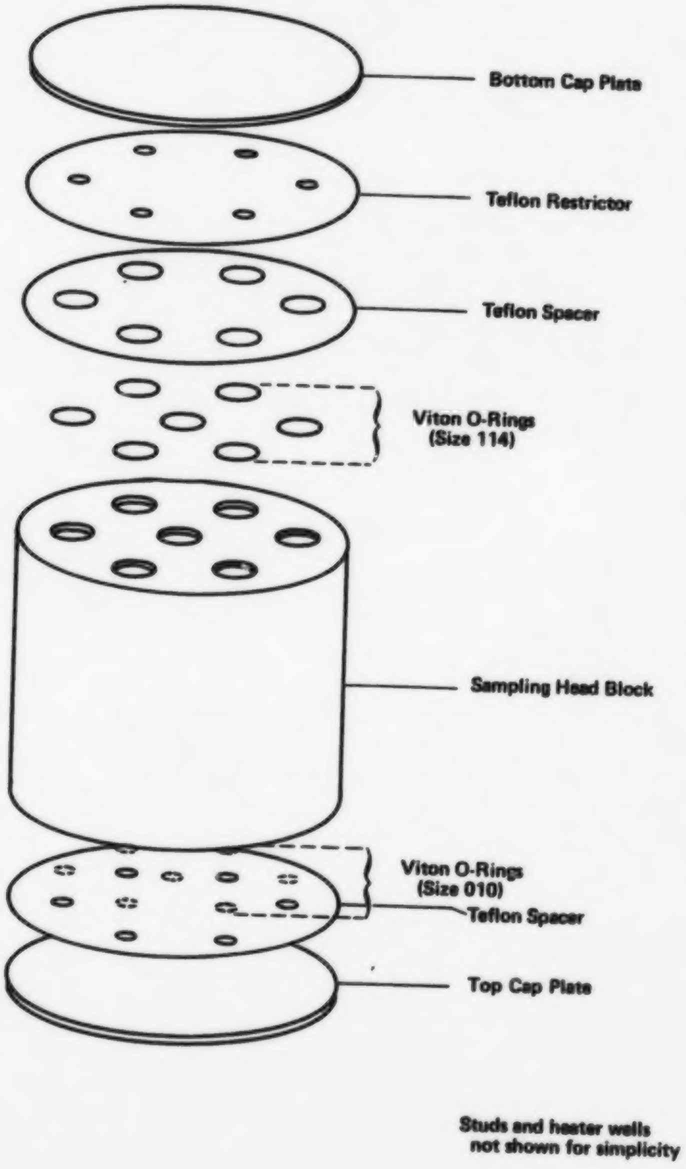

Bottom Cap Plate
Teflon Restrictor
Teflon Spacer
Viton O-Rings
(Size 114)
Sampling Head Block
Viton O-Rings
(Size 010)
Teflon Spacer
Top Cap Plate
Studs and heater wells
not shown for simplicity

Figure 65. Exploded view of sampling head block for transportation/ storage mode (upside down).

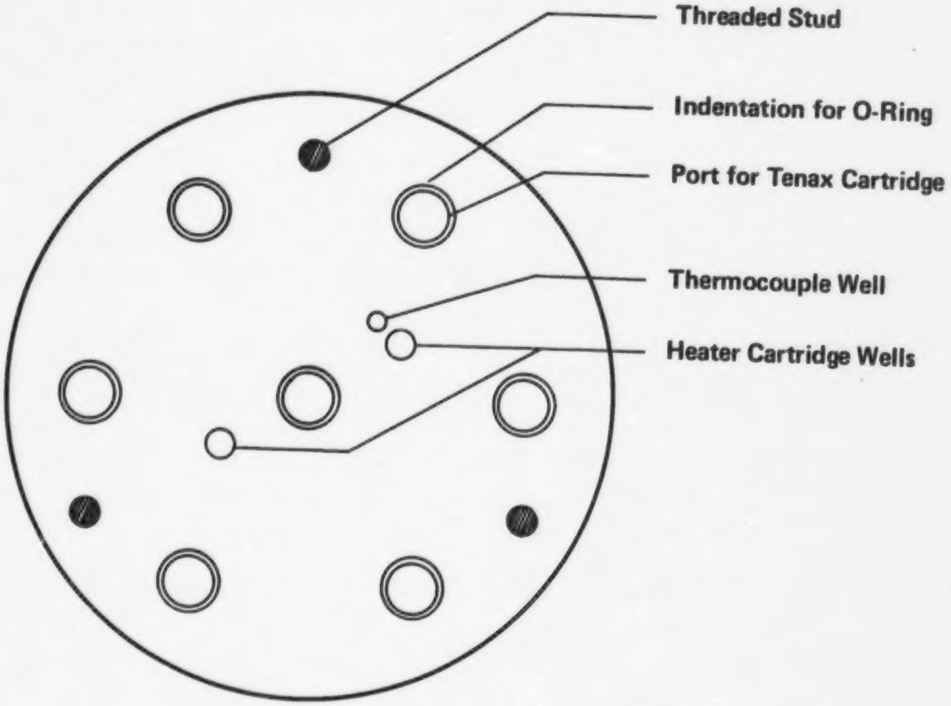

Threaded Stud
Indentation for O-Ring
Port for Tenax Cartridge
Thermocouple Well
Heater Cartridge Wells

Figure 66. View of top of sample head block - approximately to scale.

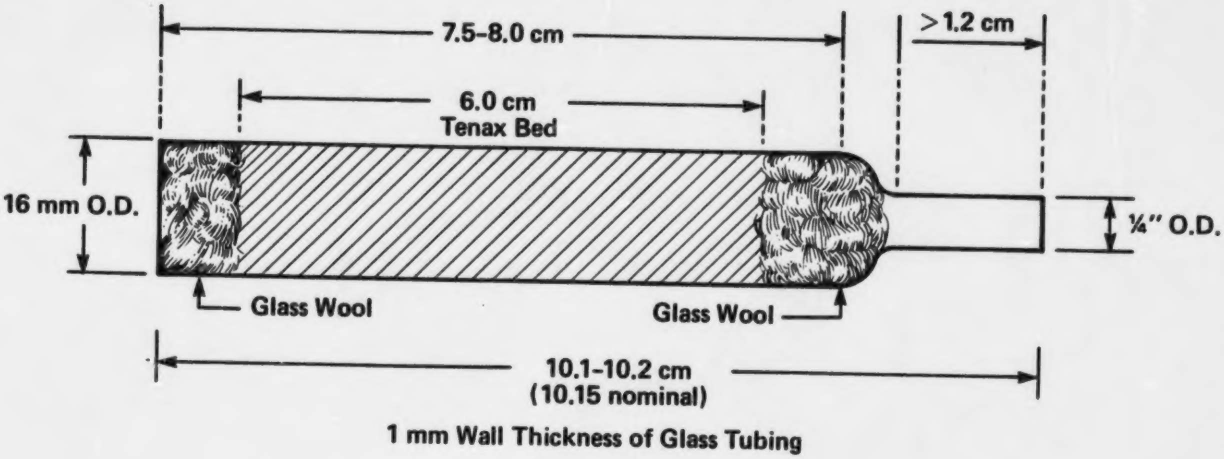

7.5-8.0 cm
>1.2 cm
6.0 cm
Tenax Bed
16 mm O.D.
¼" O.D.
Glass Wool
Glass Wool
10.1-10.2 cm
(10.15 nominal)
1 mm Wall Thickness of Glass Tubing

Figure 67. Tenax cartridges for automatic sampler.

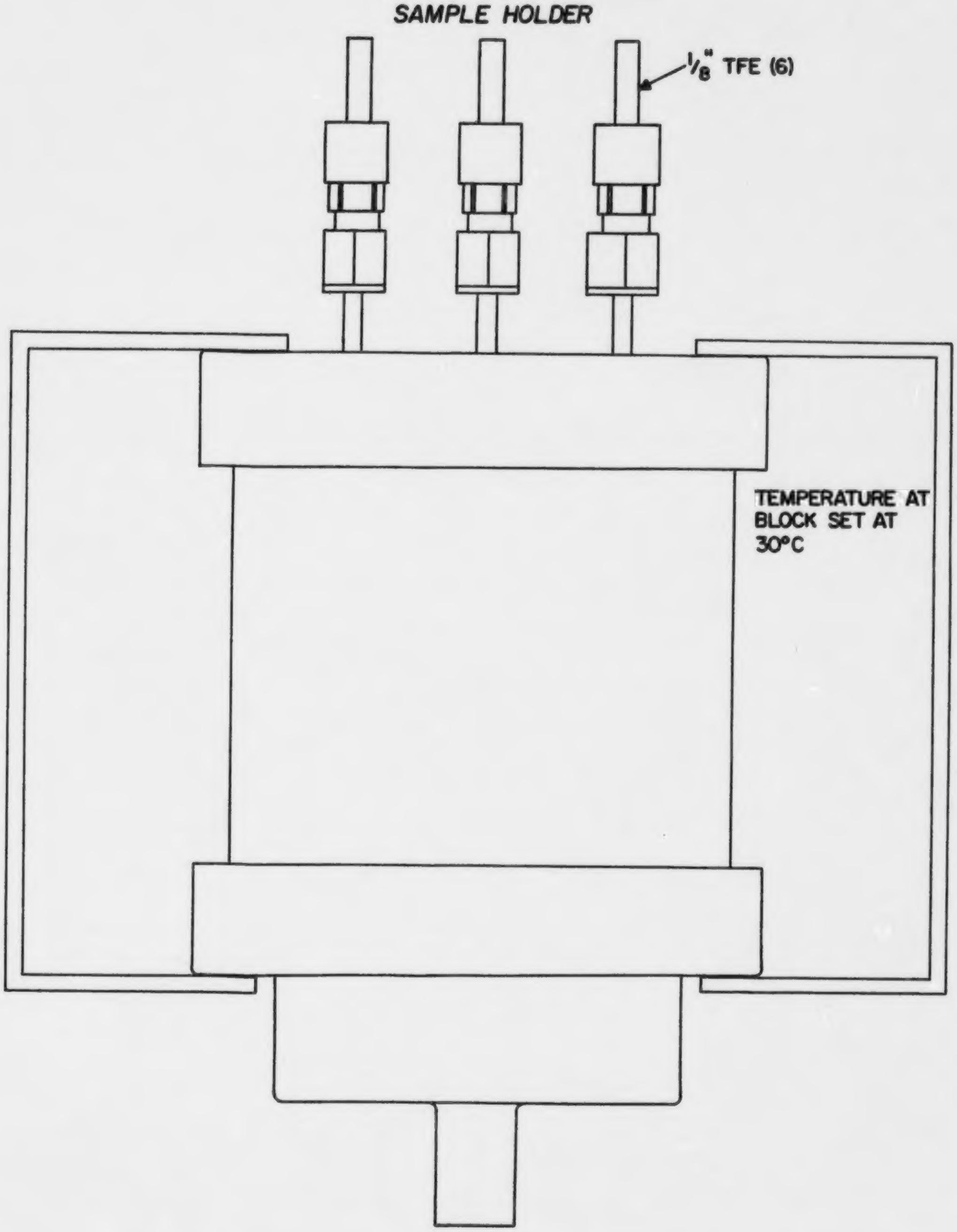

SAMPLE HOLDER
1/8" TFE (6)
TEMPERATURE AT
BLOCK SET AT
30°C

Figure 68. Sample holder.

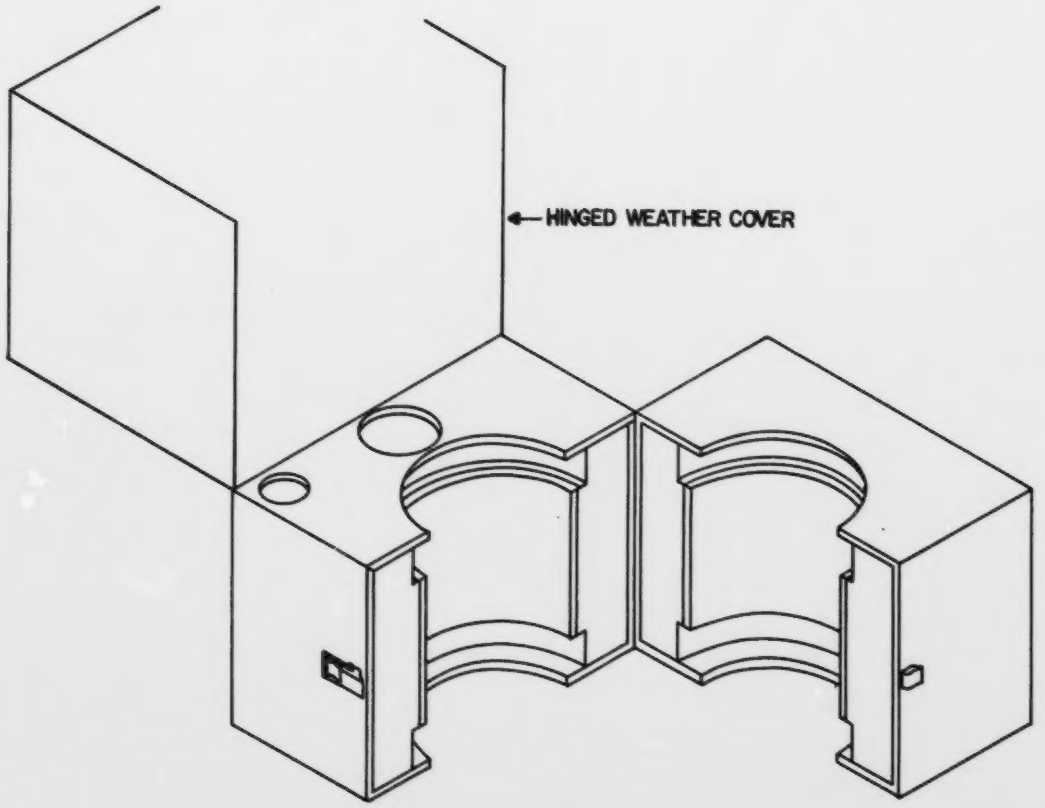
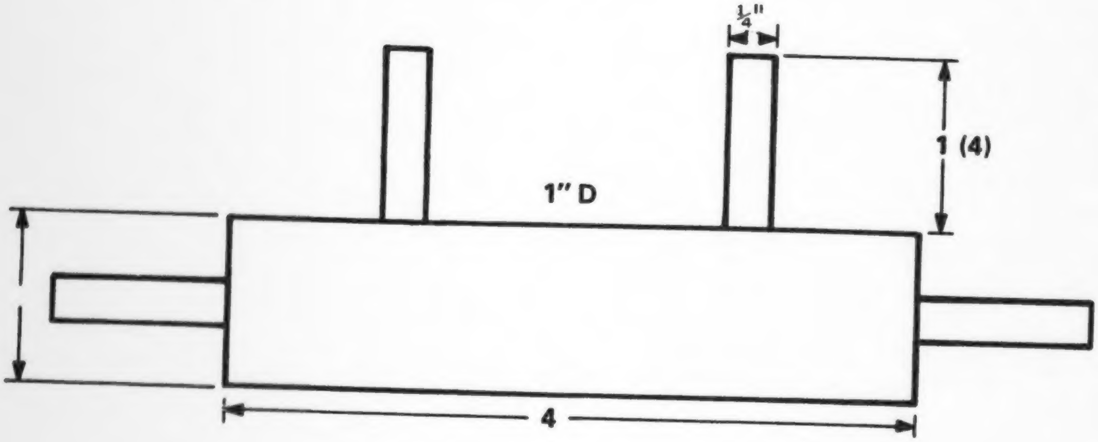

HINGED WEATHER COVER

Figure 69. Heated sample cover for sample cartridge collector.



Matl: stainless steel

Figure 70. 4-Port manifold.

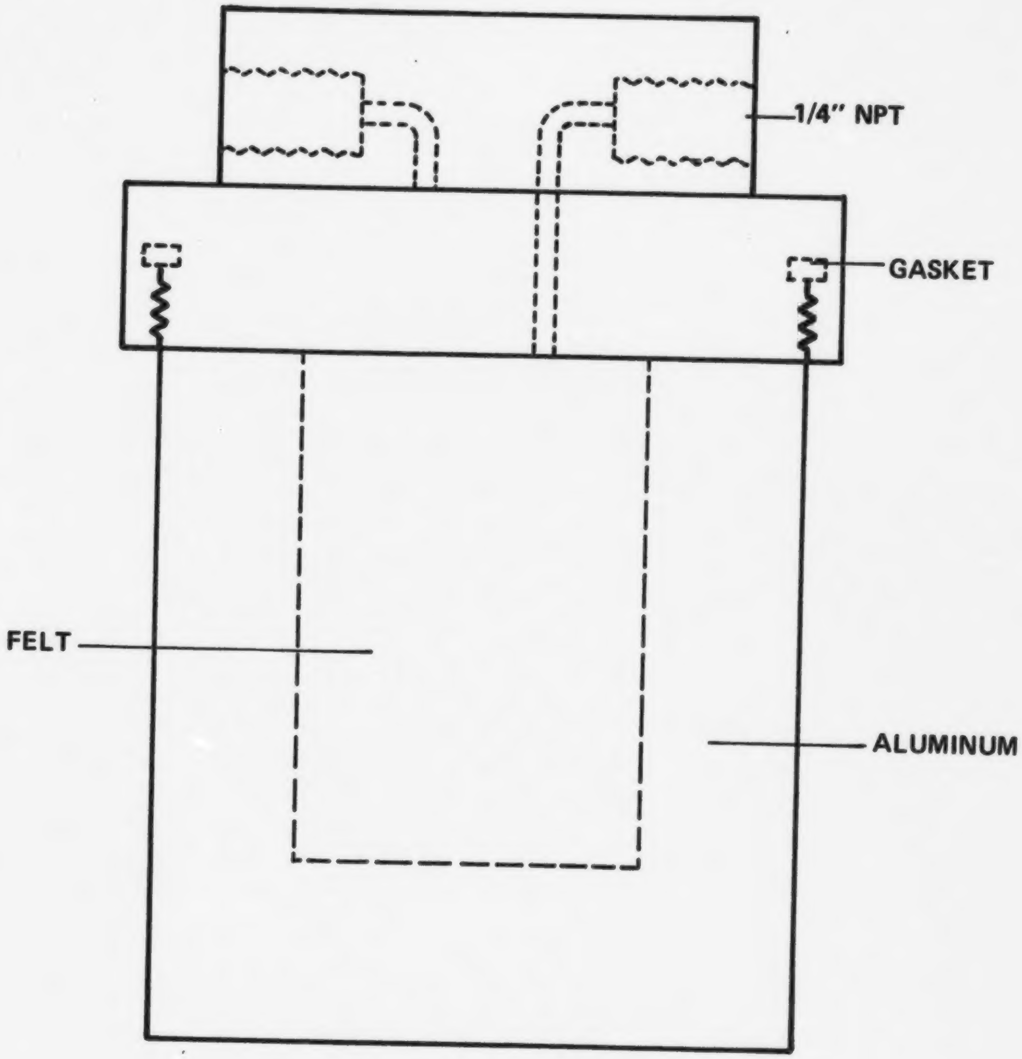

1/4" NPT
GASKET
FELT
ALUMINUM

Figure 71. Muffler.

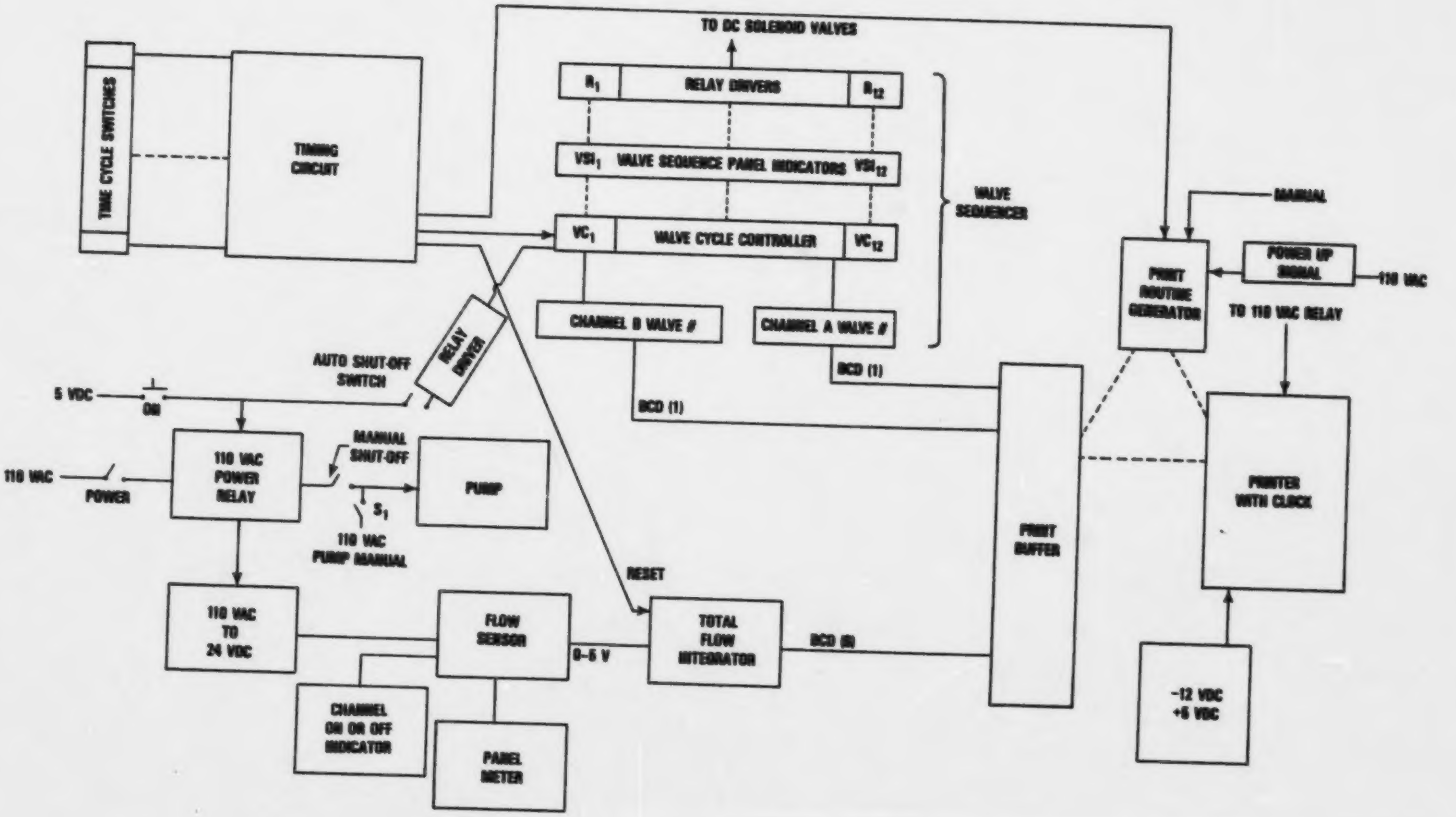

TIME CYCLE SWITCHES
TIMING CIRCUIT
TO DC SOLENOID VALVES
R_1
RELAY DRIVERS
R_{12}
VSI_1
VALVE SEQUENCE PANEL INDICATORS
VSI_{12}
VC_1
VALVE CYCLE CONTROLLER
VC_{12}
VALVE SEQUENCER
CHANNEL B VALVE #
CHANNEL A VALVE #
BCD (1)
BCD (1)
RELAY DRIVER
AUTO SHUT-OFF SWITCH
5 VDC
ON
110 VAC
POWER
110 VAC POWER RELAY
MANUAL SHUT-OFF
S_1
110 VAC PUMP MANUAL
PUMP
RESET
110 VAC TO 24 VDC
FLOW SENSOR
0–5 V
TOTAL FLOW INTEGRATOR
BCD (8)
CHANNEL ON OR OFF INDICATOR
PANEL METER
PRINT BUFFER
MANUAL
PRINT ROUTINE GENERATOR
POWER UP SIGNAL
110 VAC
TO 110 VAC RELAY
PRINTER WITH CLOCK
−12 VDC
+5 VDC

Figure 72. Auto sampler electronic schematic.

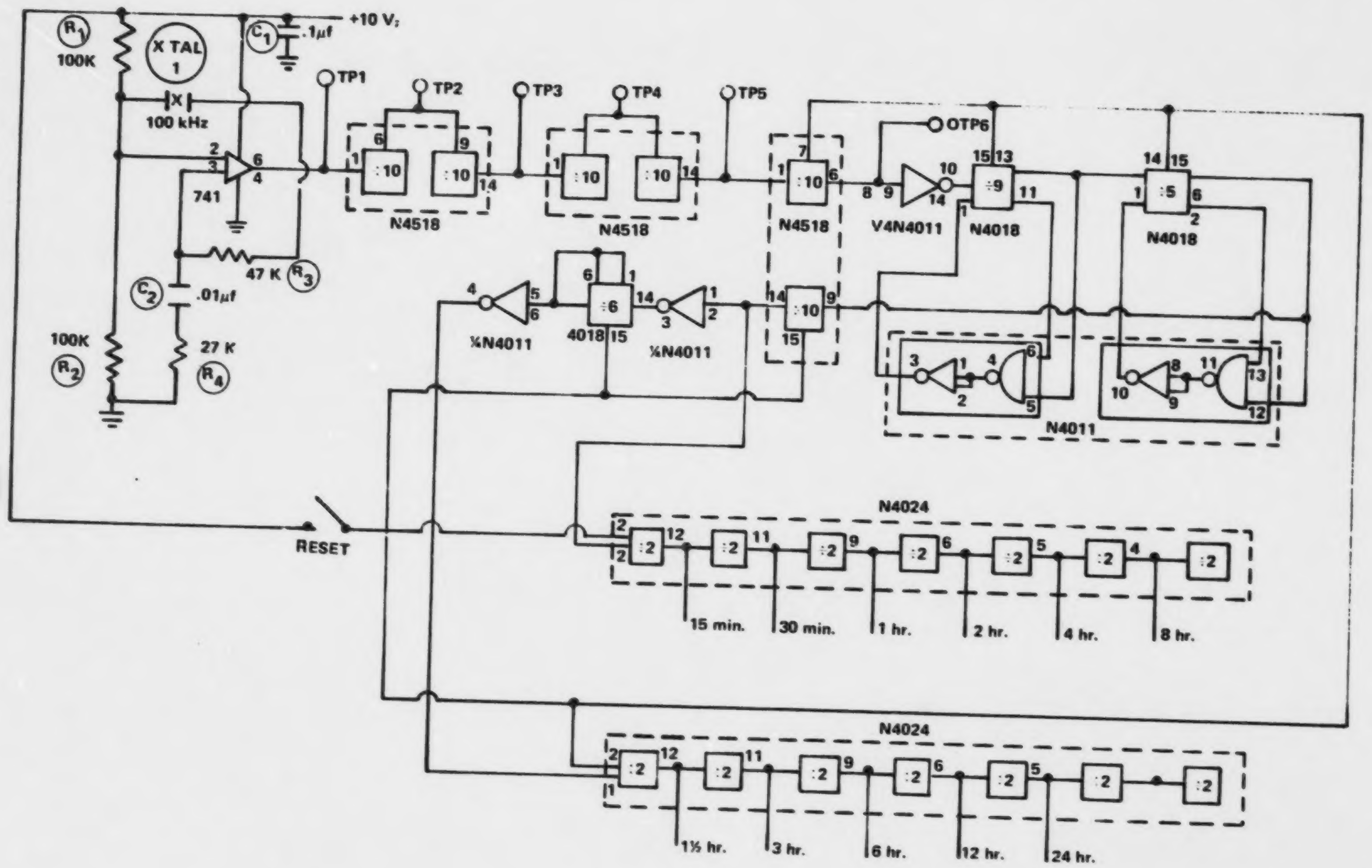

+10 V
R1
100K
X TAL 1
100 kHz
C1
.1μf
741
R3
47 K
C2
.01μf
R2
100K
R4
27 K
TP1
TP2
TP3
TP4
TP5
OTP6
N4518
N4518
N4518
V4N4011
N4018
N4018
¼N4011
4018
¼N4011
N4011
RESET
N4024
15 min.
30 min.
1 hr.
2 hr.
4 hr.
8 hr.
N4024
1½ hr.
3 hr.
6 hr.
12 hr.
24 hr.

Figure 73. Time pulse generator.

pulse at various points along the pulse dividing network. The time pulse initiates the Print Routine Generator, advances the Valve Cycle Controller and resets the Total Flow Integrator.

The Total Flow Rate Indicator (Fig. 74) consists of a voltage to frequency converter with an output of 1000 pulses per second per volt input. The calibration of the flow sensor will typically be 11 amp per volt. Based on this ratio the pulse output is divided by 600 to give an output of 0.01 liter in the least significant and 1000.00 liter in the most significant digit. These six digits are fed into the print buffer. In addition the flow rate senor dives a panel meter to indicate the instantaneous flow rate.

The Valve Cycle Controller (Fig. 75) is basically a shift register (Fig. 76) which advances one position with each time pulse. It is arranged in two units corresponding to the duplicate channels A and B so that they can be advanced in parallel (with one line on each channel open) or in series (with the first line of channel B following the completion of sampling on the last line of channel A). Upon receiving the signal from the shift register (Fig. 76), relay drivers provide power to solenoid valves controlling flow thru appropriate sample lines. An open valve is indicated by LED on the front panel and also transferred in BCD format to the print buffer (Fig. 77).

At each time pulse a print routine is initiated. The printer prints time of day and date followed by the information in the print buffer, i.e., sample volume and sample lines being sampled. At the conclusion of sampling the Valve Cycle Controller deactivates the pumping system and turns the sampler off. Remaining pertinent circuits are depicted in Figures 78-85.

The fabrication of the automatic sampler also included the following additional features:

(1) A cooling fan was installed behind the pump to reduce potential overheating.

(2) A manual channel stepping switch and 9 sec stepping function was installed on the front panel. This feature aids the checking of all solenoid valve switching operations and instrument flow calibration.

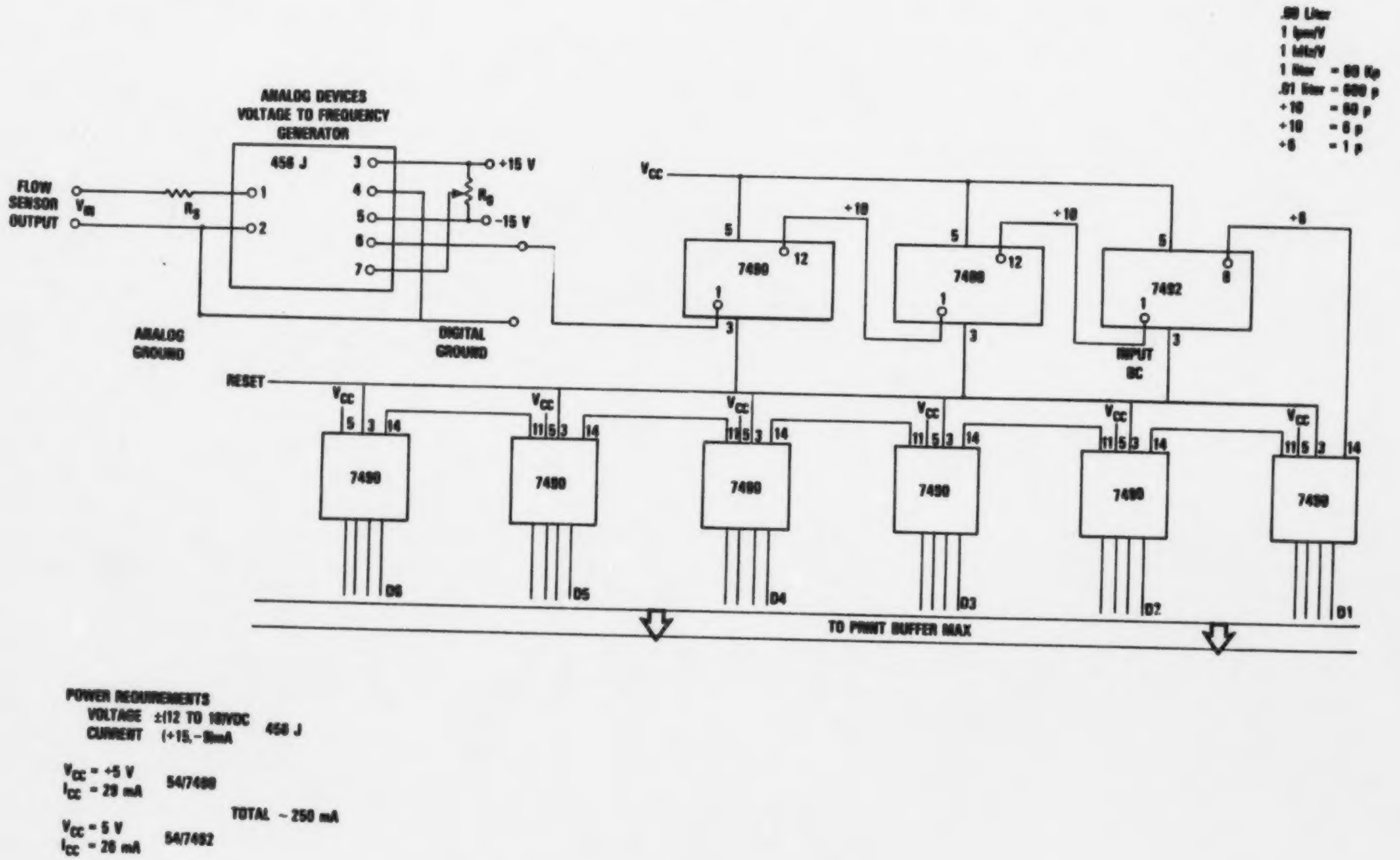

ANALOG DEVICES VOLTAGE TO FREQUENCY GENERATOR
456 J
1
2
3
4
5
6
7
+15 V
-15 V
R_0
R_S
FLOW SENSOR OUTPUT
V_{in}
ANALOG GROUND
DIGITAL GROUND
V_{CC}
RESET
7490
7490
7492
5
12
1
3
÷10
÷10
÷6
6
INPUT BC
11
14
D6
D5
D4
D3
D2
D1
TO PRINT BUFFER MAX
.50 Liter
1 lpm/V
1 kHz/V
1 liter = 60 Kp
.01 liter = 600 p
÷10 = 60 p
÷10 = 6 p
÷6 = 1 p
POWER REQUIREMENTS
VOLTAGE ±(12 TO 18)VDC
CURRENT (+15, -8)mA
456 J
V_{CC} = +5 V
I_{CC} = 29 mA
54/7490
TOTAL ~ 250 mA
V_{CC} = 5 V
I_{CC} = 28 mA
54/7492

Figure 74. Flow rate integrator.

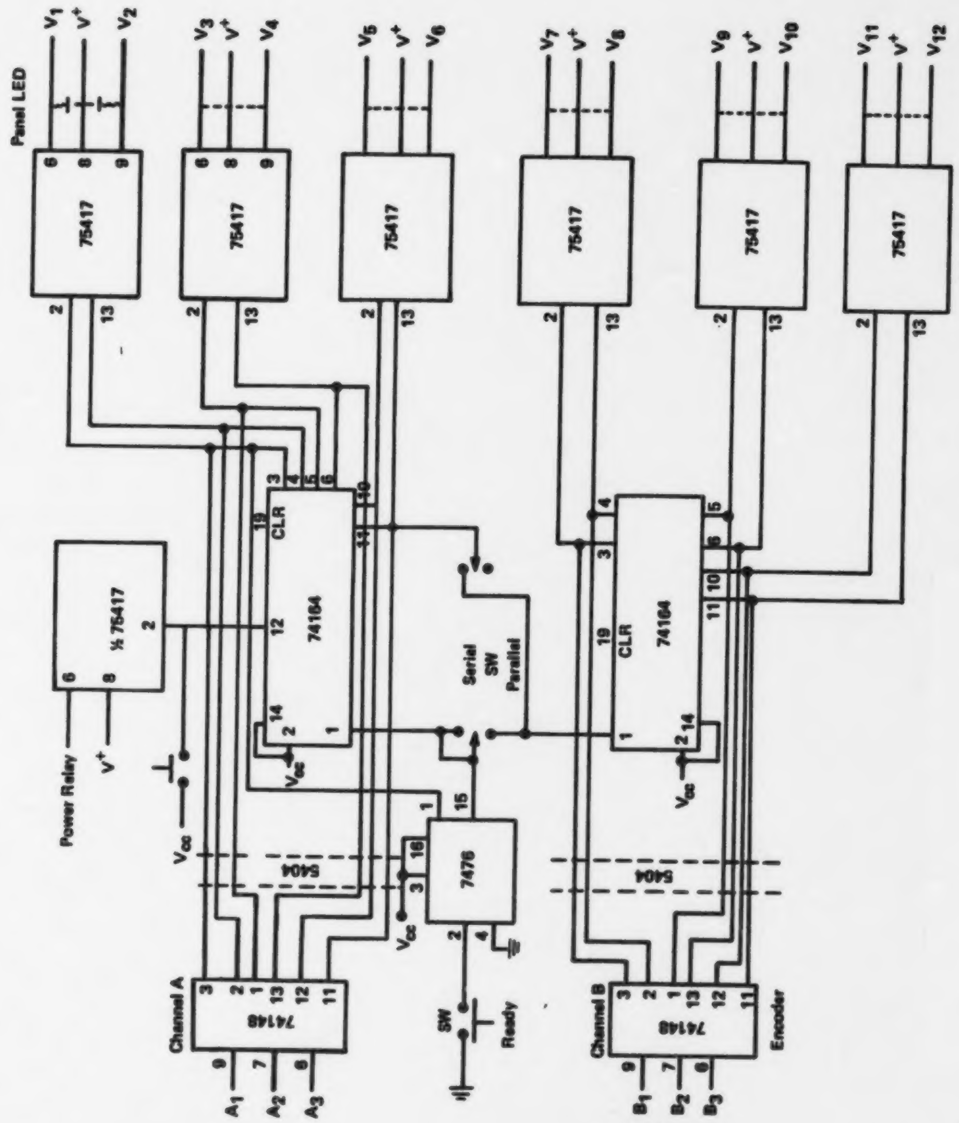

Panel LED
V_1
V^+
V_2
V_3
V_4
V_5
V_6
V_7
V_8
V_9
V_{10}
V_{11}
V_{12}
75417
Relay Driver
½ 75417
Power Relay
V_{cc}
74164
CLR
Serial
SW
Parallel
7476
5404
Channel A
Channel B
74148
Encoder
A_1
A_2
A_3
B_1
B_2
B_3
To Print Buffer
SW
Ready

Figure 75. Valve sequencer.

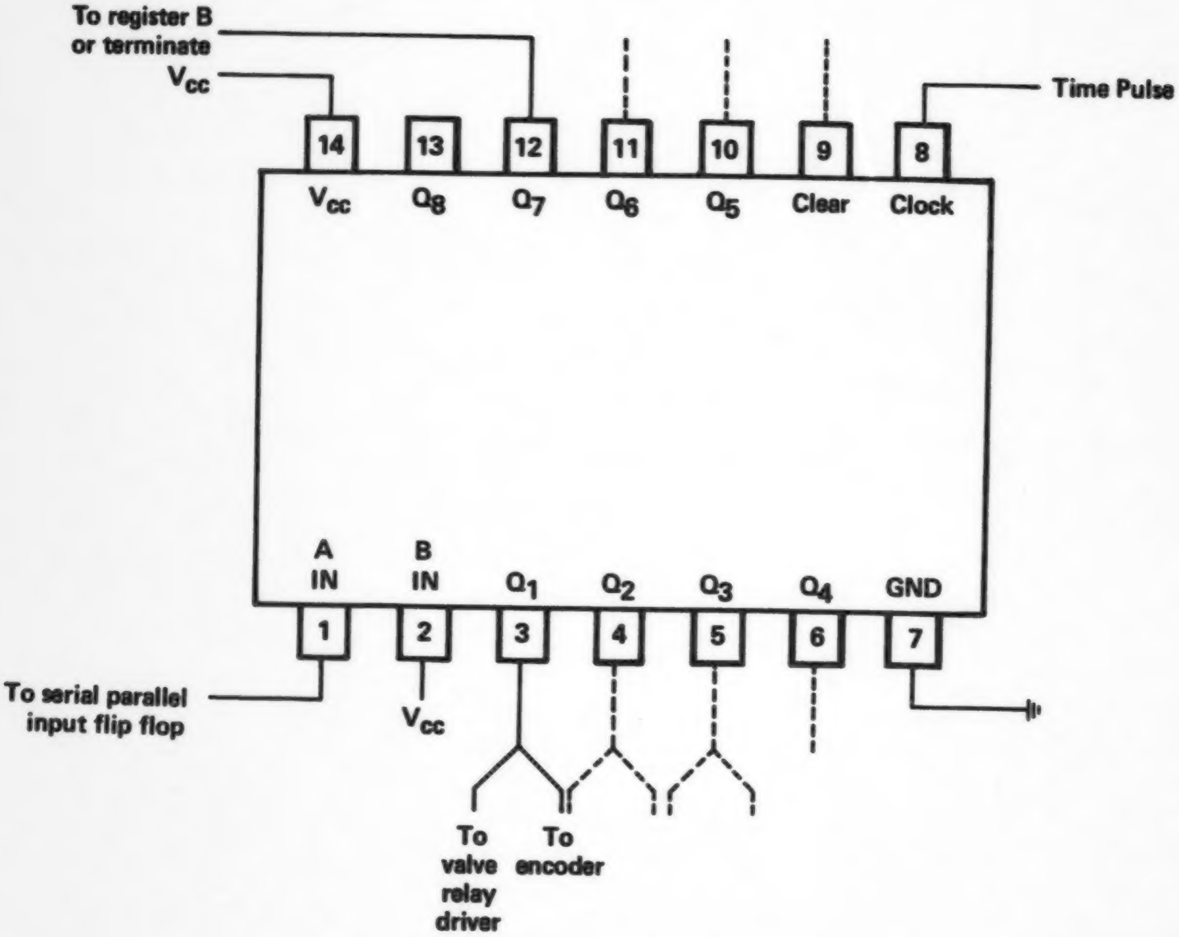
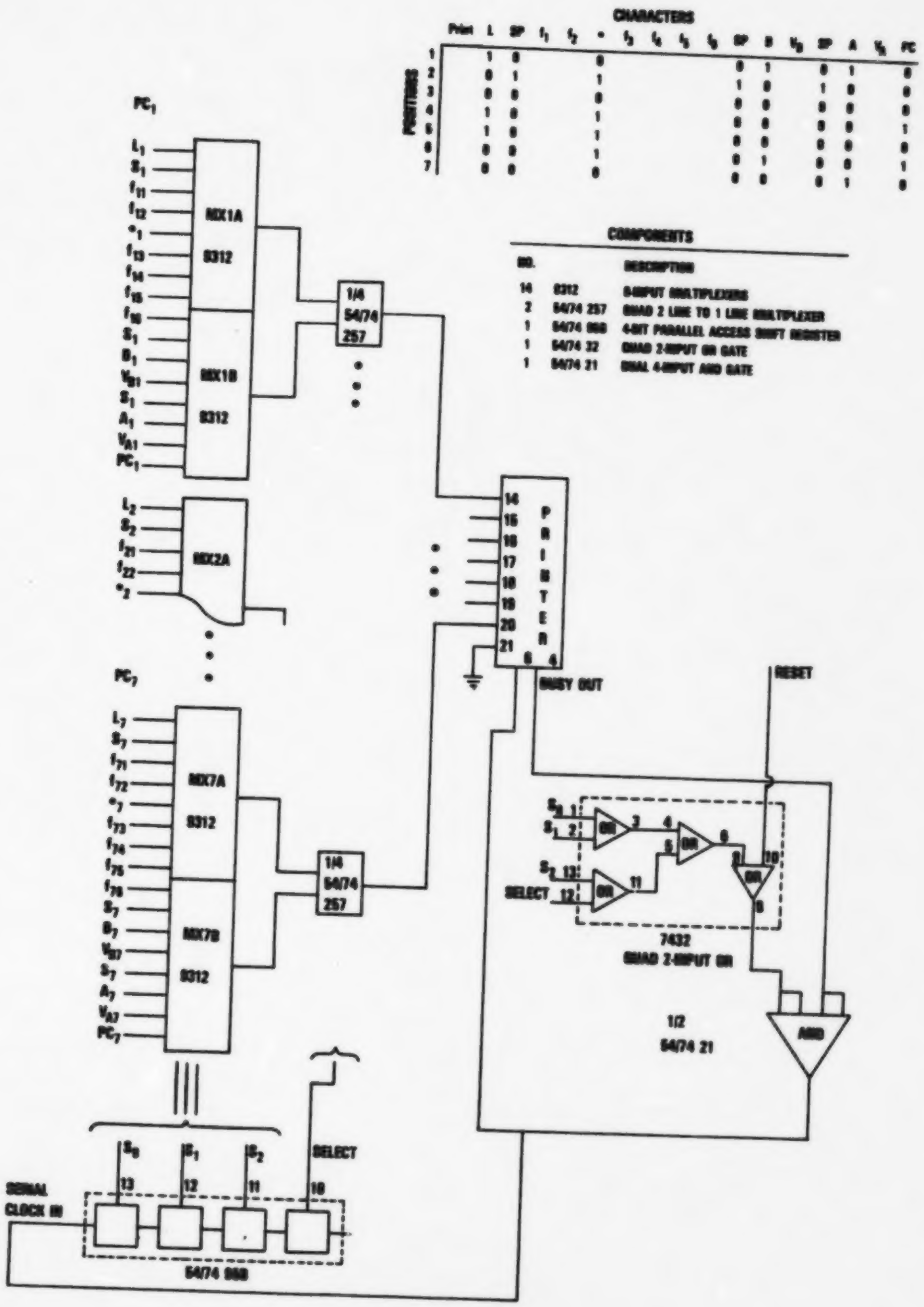

To register B or terminate
V_{cc}
Time Pulse
14
13
12
11
10
9
8
V_{cc}
Q_8
Q_7
Q_6
Q_5
Clear
Clock
A IN
B IN
Q_1
Q_2
Q_3
Q_4
GND
1
2
3
4
5
6
7
To serial parallel input flip flop
V_{cc}
To valve relay driver
To encoder

Figure 76. 74164 8-Bit parallel-out serial shift register.


CHARACTERS
Print L SP f_1 f_2 • f_3 f_4 f_5 f_6 SP B V_B SP A V_A PC
POSITIONS
1 2 3 4 5 6 7
PC_1
L_1
S_1
f_{11}
f_{12}
$•_1$
f_{13}
f_{14}
f_{15}
f_{16}
S_1
B_1
V_{B1}
S_1
A_1
V_{A1}
PC_1
MX1A
9312
MX1B
9312
1/4
54/74
257
L_2
S_2
f_{21}
f_{22}
$•_2$
MX2A
PC_7
L_7
S_7
f_{71}
f_{72}
$•_7$
f_{73}
f_{74}
f_{75}
f_{76}
S_7
B_7
V_{B7}
S_7
A_7
V_{A7}
PC_7
MX7A
9312
MX7B
9312
1/4
54/74
257
14
15
16
17
18
19
20
21
6
4
P R I N T E R
BUSY OUT
RESET
S_0 1
S_1 2
S_2 13
SELECT 12
OR
OR
OR
OR
3
4
5
6
8
9
10
11
7432
QUAD 2-INPUT OR
1/2
54/74 21
AND
S_0
S_1
S_2
SELECT
13
12
11
10
SERIAL
CLOCK IN
54/74 968

COMPONENTS

NO.		DESCRIPTION
14	9312	8-INPUT MULTIPLEXERS
2	54/74 257	QUAD 2 LINE TO 1 LINE MULTIPLEXER
1	54/74 968	4-BIT PARALLEL ACCESS SHIFT REGISTER
1	54/74 32	QUAD 2-INPUT OR GATE
1	54/74 21	DUAL 4-INPUT AND GATE

Figure 77. Printer interface buffer.

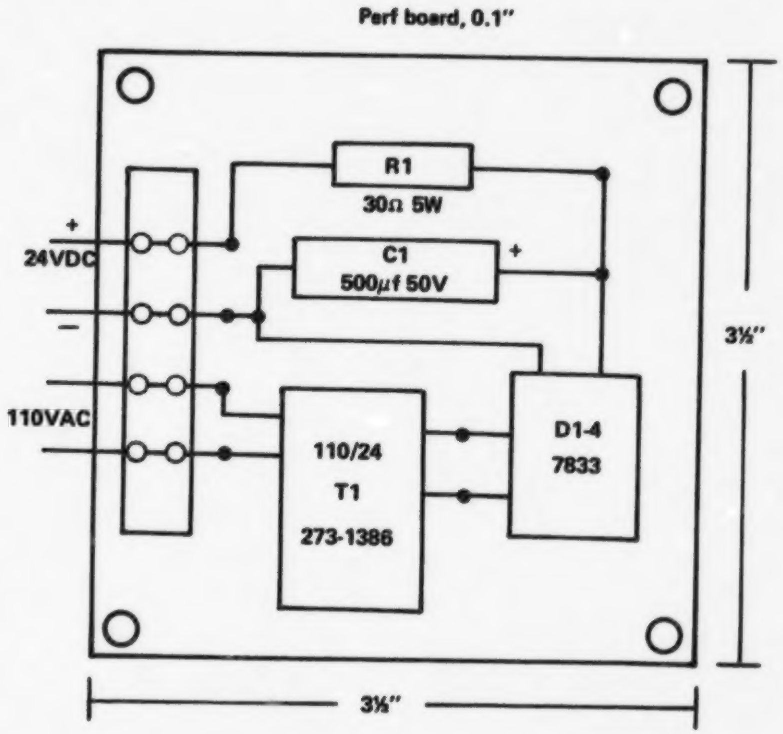

Perf board, 0.1"
R1
30Ω 5W
C1
500µf 50V
+
+
24VDC
–
110VAC
110/24
T1
273-1386
D1-4
7833
3½"
3½"

Figure 78. Flow sensor power supply.

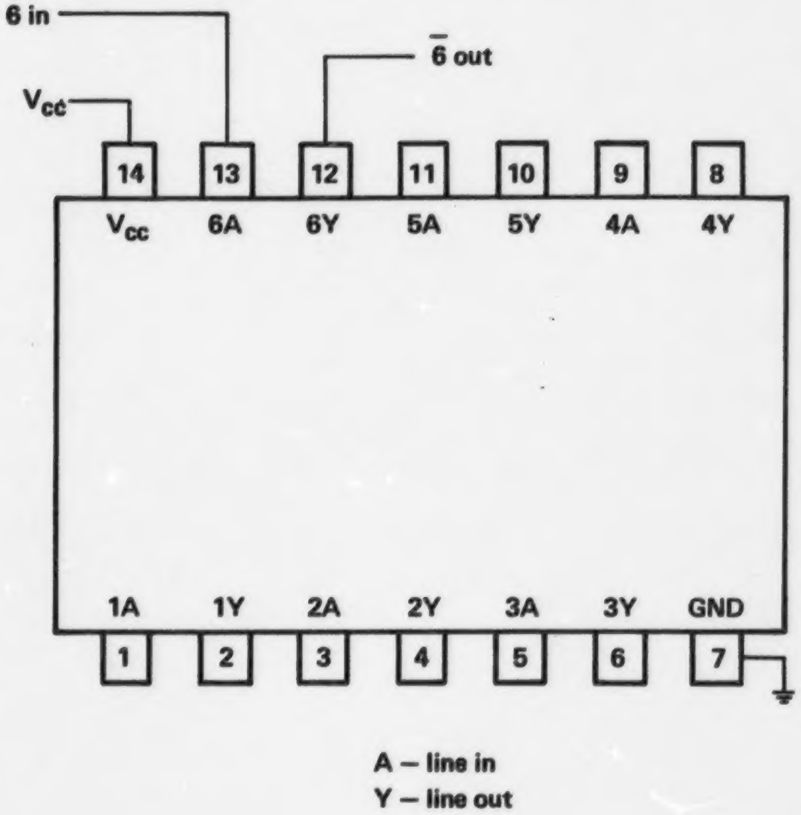

6 in
$\overline{6}$ out
V_{cc}
14
13
12
11
10
9
8
V_{cc}
6A
6Y
5A
5Y
4A
4Y
1A
1Y
2A
2Y
3A
3Y
GND
1
2
3
4
5
6
7
A – line in
Y – line out

Figure 79. 7404 Hex inverter.

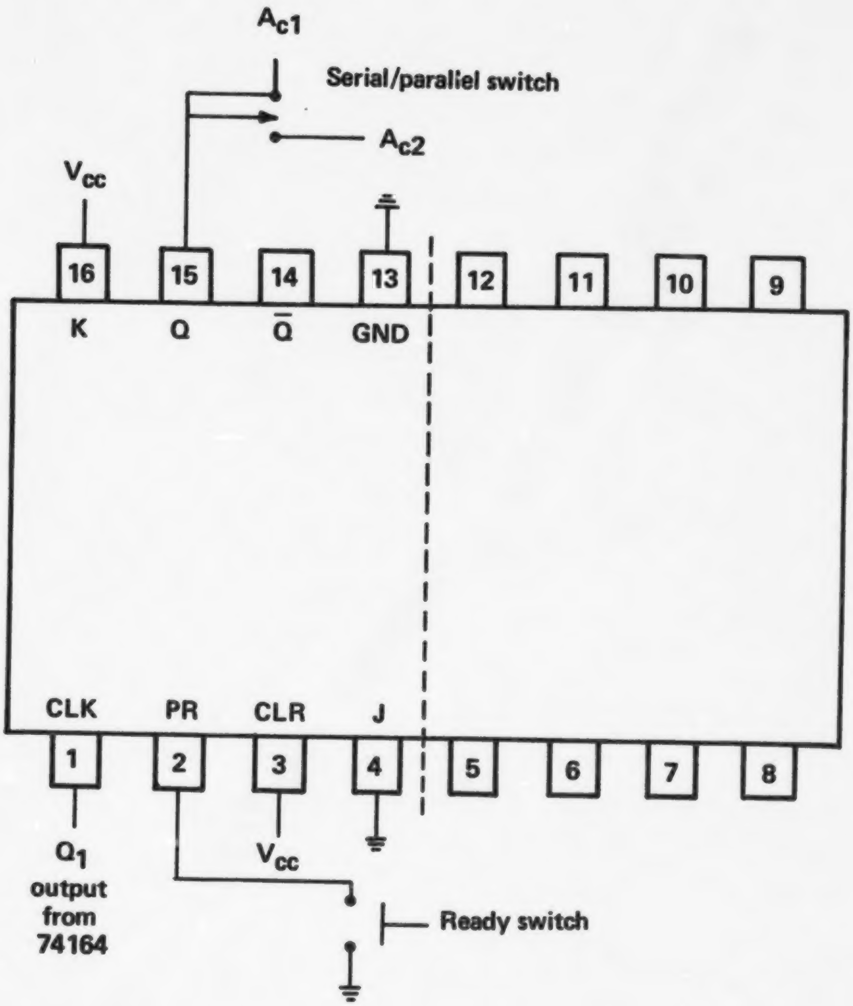
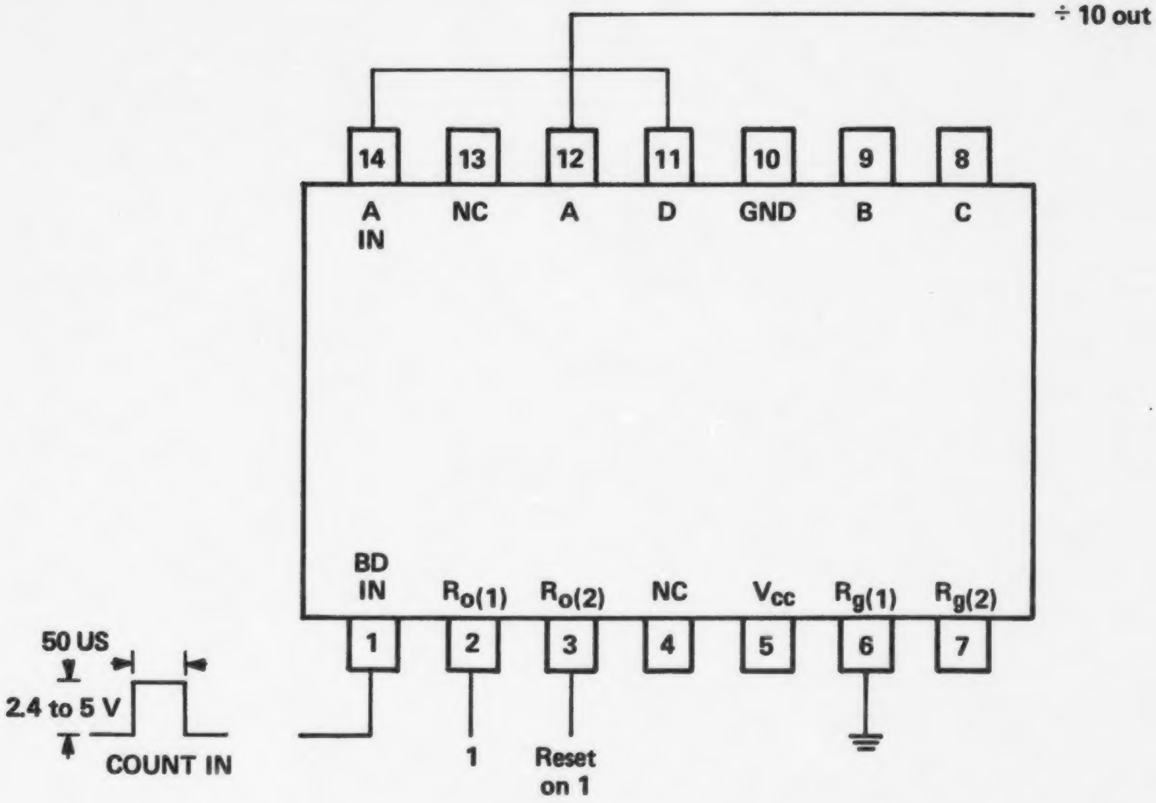
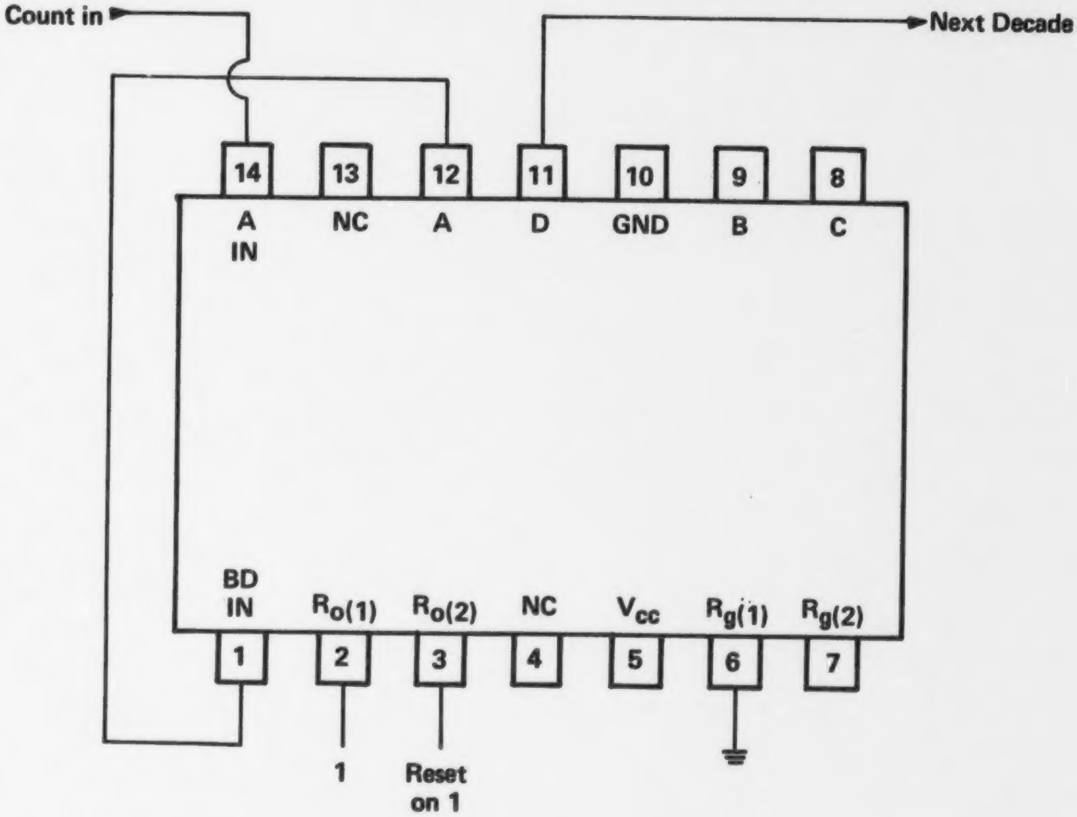

A_{c1}
Serial/parallel switch
A_{c2}
V_{cc}
16
15
14
13
12
11
10
9
K
Q
$\overline{Q}$
GND
CLK
PR
CLR
J
1
2
3
4
5
6
7
8
Q_1
output
from
74164
V_{cc}
Ready switch

Figure 80. 7476 Dual JK flip flop with preset and clear.



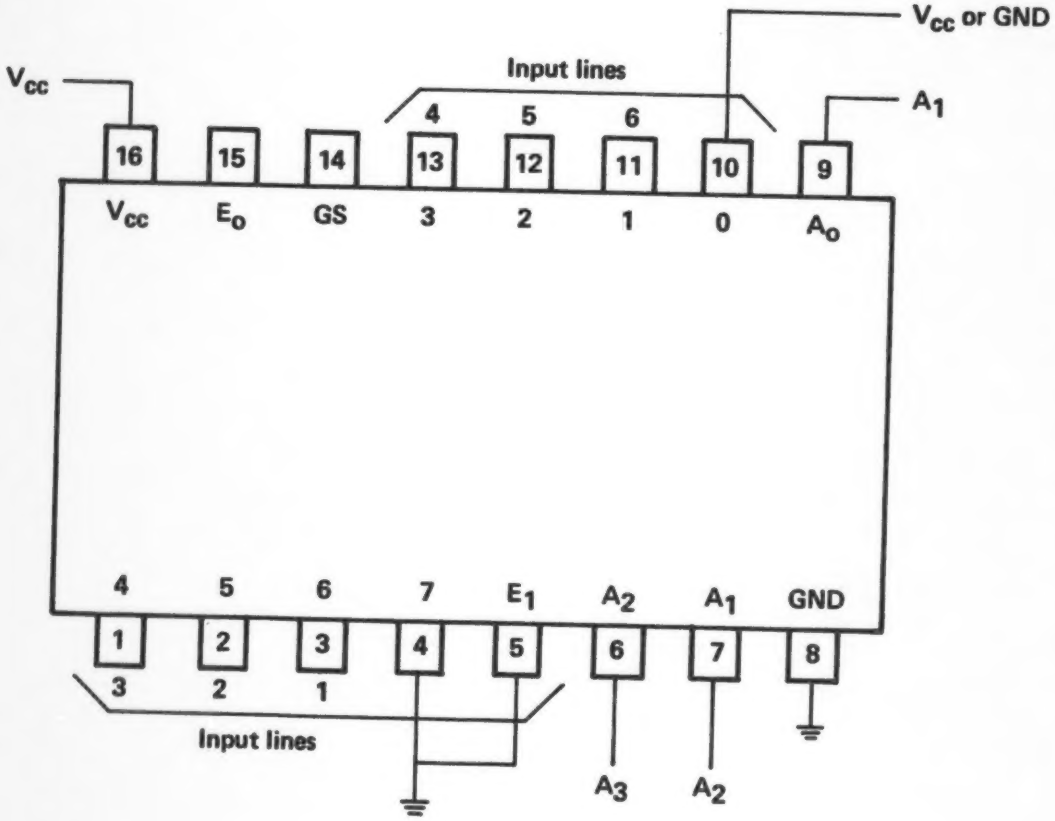
÷ 10 out
14
13
12
11
10
9
8
A IN
NC
A
D
GND
B
C
BD IN
$R_o(1)$
$R_o(2)$
NC
V_{cc}
$R_g(1)$
$R_g(2)$
1
2
3
4
5
6
7
50 US
2.4 to 5 V
COUNT IN
1
Reset on 1

Figure 81. 7490 Decade counter as divided by 10.


Count in
Next Decade
14
13
12
11
10
9
8
A
IN
NC
A
D
GND
B
C
BD
IN
Ro(1)
Ro(2)
NC
Vcc
Rg(1)
Rg(2)
1
2
3
4
5
6
7
1
Reset
on 1

Possible alternate 8285

Figure 82. 7490 Decade counter in cascade.



V_cc
Input lines
V_cc or GND
A_1
4
5
6
16
15
14
13
12
11
10
9
V_cc
E_o
GS
3
2
1
0
A_o
4
5
6
7
E_1
A_2
A_1
GND
1
2
3
4
5
6
7
8
3
2
1
Input lines
A_3
A_2

Figure 83. 74148 8-Line to 3-line encoder.

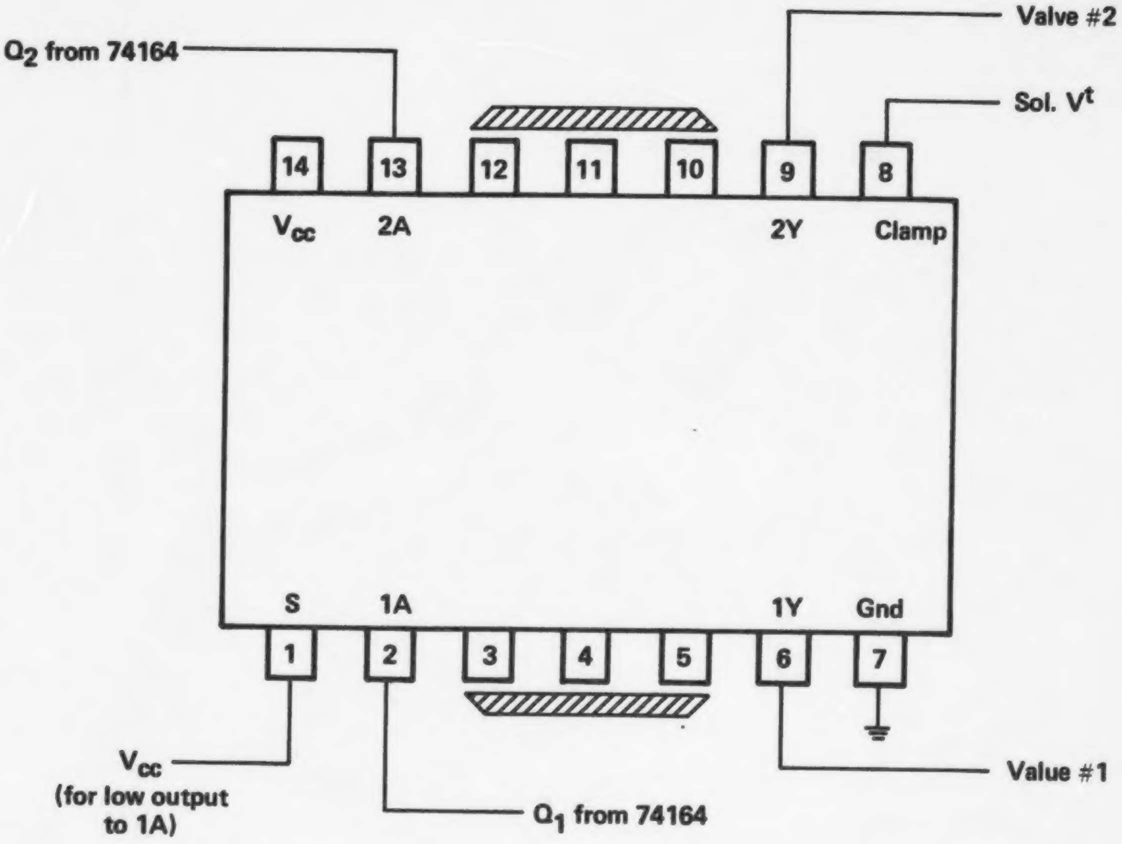

Q2 from 74164
Valve #2
Sol. Vt
14
13
12
11
10
9
8
Vcc
2A
2Y
Clamp
S
1A
1Y
Gnd
1
2
3
4
5
6
7
Vcc
(for low output to 1A)
Q1 from 74164
Value #1

Figure 84. ʼ 75417 Dual peripheral driver.

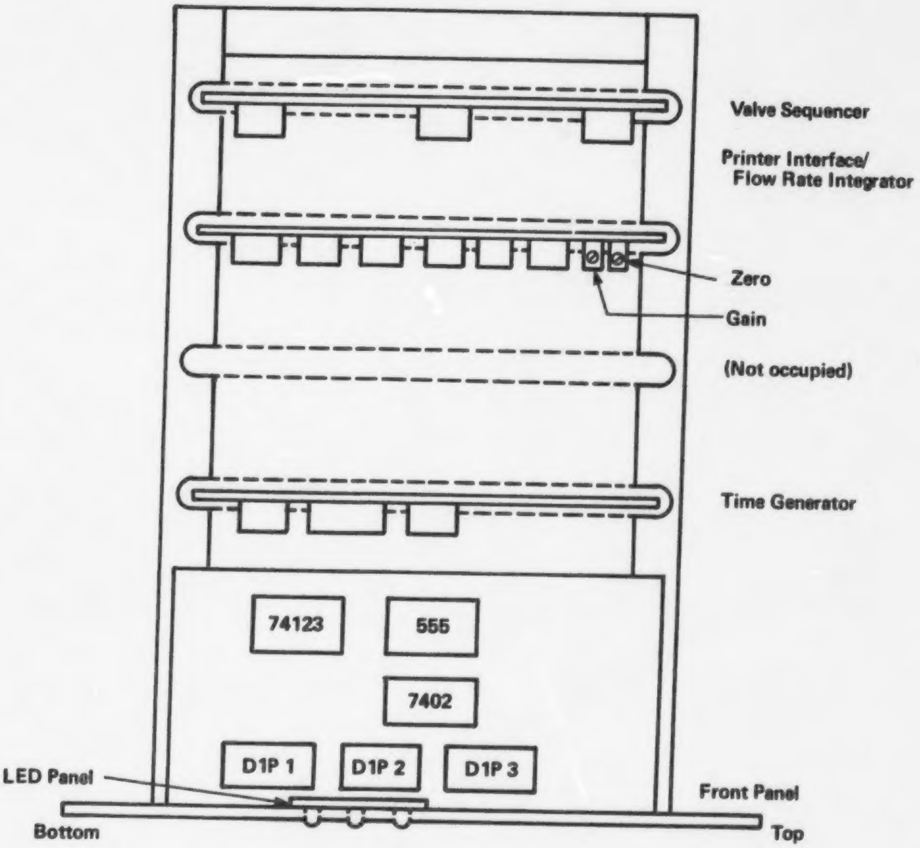

Valve Sequencer
Printer Interface/ Flow Rate Integrator
Zero
Gain
(Not occupied)
Time Generator
74123
555
7402
D1P 1
D1P 2
D1P 3
LED Panel
Front Panel
Bottom
Top

Figure 85. Arrangement of P.C. boards on edgecard frame (looking into connectors).

(4) The sampler was equipped with two calibration ports with 0.25 in quick-connect assess. They were tied into the flow at each channel before the manual flow control valves. This feature facilitates presetting the flow rates as well as calibrating the flow meter.

and (5) Addition of noise suppression steps to improve the timing and valve realiability.

SECTION 9

PERFORMANCE OF AUTOMATIC SAMPLER

EVALUATION OF STEPPING SEQUENCER AND SAMPLER CALIBRATION

The Nutech automatic sampler was tested in both parallel and serial modes to determine whether the sampler was stepping through each channel in the proper order. The sampler was tested for sampling periods at 15 min, 30 min, 45 min, 1 hr, 2 hr, 12, 24 hr and was found to be stepping through the channels correctly at the proper time intervals.

The samplers digital flow meter was calibrated to read the actual flow rate being sampled by adjusting zero and gain controls to the digital flow meter. The sampler was then tested to determine if all selonoids were functioning properly to allow for sampling through the 12 sampling ports. Tests revealed all sampling ports were functioning properly. The sampler was then tested to ensure that the flow set on the digital flow meter corresponded to the actual flow (as measured by an NBS bubble meter). The results of these tests are given in Tables 71 and 72. These experiments revealed that the sampler set flow and actual flow agree within 2%. The integrator was then checked to see if the data printout agreed with the actual volume being sampled. Initially, the integration was found to deviate 20% in the serial mode and 3-5% in the parallel mode. Table 73 lists the calibration results. Table 74 gives the comparison of set point and actual flow vs the dynamic range.

The sampler was then also tested to reveal if the digital flow meter would drift from the actual flow rate being sampled over long periods of time. The test revealed that no significant drift was present (Tables 75 and 76).

EVALUATION OF SAMPLING HEADS

Initial experiments included determining the sealing capabilities of two prototype sampling heads. One head utilizes a phenolic screw cap to

Table 71. FLOW METER CALIBRATION OF AUTOMATIC SAMPLER - SERIAL/MANUAL MODE

	Channel A		Channel B	
Port No.	Set Point	Actual	Set Point	Actual
1	406	398.9	421	418.5
2	406	399.6	421	418.5
3	406	400.7	421	417.4
4	406	400.0	421	418.8
5	406	398.7	421	419.1
6	406	400.0	421	417.7
	Mean	399.6	Mean	418.2
	S.D.	0.75	S.D.	0.80
	% S.D.	0.19	% S.D.	0.19
% Dev. from Set Point		1.56		0.66

[a] Checked with NBS bubble meter, mL/min.

Table 72. FLOW METER CALIBRATION OF AUTOMATIC SAMPLER - PARALLEL/MANUAL MODE

	Channel A		B		A + B	
Port No.	Set Point	Actual[a]	Set Point	Actual	Set Point	Actual
1	301	295.2	306	295.4	587	590.6
2	301	296.0	306	296.3	587	592.3
3	301	295.9	306	298.4	579	594.3
4	301	301.5	306	295.2	586	596.7
5	301	294.9	306	303.1	595	598.0
6	301	293.3	306	309.9	599	603.2
Mean		296.1		299.7		595.8
S.D.		2.80		5.79		4.52
%S.D.		0.95		1.93		0.76
% Dev. from Set Point		1.62		2.05		1.12

[a] Checked by NBS bubble meter, mL/min.

Table 73. FLOW INTEGRATOR CALIBRATION OF AUTOMATIC SAMPLER - PARALLEL/MANUAL MODE

	Channel A + B				
Port No.	Set Point	Actual[a]	Integrator Total (ℓ)	Set Point Total (ℓ)	Actual Total (ℓ)
1	587	590.6	-	-	-
2	587	592.3	2.88	2.94	2.96
3	579	594.3	2.87	2.90	2.97
4	586	596.7	2.88	2.93	2.98
5	595	598.0	2.95	2.98	2.99
6	599	603.2	2.97	2.99	3.02

[a] Checked with NBS bubble meter, mL/min.

Table 74. CALIBRATION OF DYNAMIC RANGE FOR FLOW METER ON AUTOMATIC SAMPLER

Channel A		Channel A		Channel B	
(8/8/80)		(8/19/80)		(8/19/80)	
Set Point	Actual	Set Point	Actual	Set Point	Actual
8	9	32	33	55	54
38	38	94	90	94	91
98	93	179	175	195	193
210	209	294	292	316	315
318	314	394	391	421	418
417	410	496	493	506	507
510	507	592	586	616	620
607	599	678	675	716	722

Table 75. AUTOMATIC SAMPLER OUTPUT-PARALLEL MODE

Time Period		
15 min	30 min	1 hr
6A 7B 0003.19 09/11 10:04	6A 6B 0012.47 09/11 13:13	6A 6B 0025.02 09/11 23:00
5A 7B 0003.19 09/11 09:49	5A 5B 0012.51 09/11 12:43	5A 5B 0025.07 09/11 22:00
4A 7B 0003.19 09/11 09:34	4A 4B 0012.32 09/11 12:13	4A 4B 0024.67 09/11 21:00
3A 7B 0003.21 09/11 09:19	3A 3B 0012.35 09/11 11:43	3A 3B 0024.66 09/11 20:00
2A 7B 0003.25 09/11 09:04	2A 2B 0012.46 09/11 11:13	2A 2B 0024.77 09/11 19:00
1A 7B 0005.01 09/11 08:49	1A 1B 0012.46 09/11 10:43	1A 1B 0024.79 09/11 16:00

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Table 76. AUTOMATIC SAMPLER OUTPUT-SERIAL MODE

Time Period			
15 min	30 min	30 min	1 hr
7A 6B 0003.20 09/08 17:04	7A 6B 0006.19 09/09 18:45	7A 6B 0006.20 09/10 03:42	7A 6B 0012.31 09/10 20:55
7A 5B 0003.20 09/08 16:49	7A 5B 0006.19 09/09 18:15	7A 5B 0006.21 09/10 03:12	7A 5B 0012.29 09/10 19:55
7A 4B 0003.19 09/08 16:34	7A 4B 0006.18 09/09 17:45	7A 4B 0006.21 09/10 02:42	7A 4B 0012.26 09/10 18:55
7A 3B 0003.20 09/08 16:19	7A 3B 0006.19 09/09 17:15	7A 3B 0006.21 09/10 02:12	7A 3B 0012.26 09/10 17:55
7A 2B 0003.20 09/08 16:04	7A 2B 0006.20 09/09 16:45	7A 2B 0006.21 09/10 01:42	7A 2B 0012.27 09/10 16:55
7A 1B 0003.23 09/08 15:49	7A 1B 0006.24 09/09 16:15	7A 1B 0006.25 09/10 01:12	7A 1B 0012.32 09/10 15:55
6A 7B 0003.17 09/08 15:34	6A 7B 0006.34 09/09 15:45	6A 7B 0006.37 09/10 00:42	6A 7B 0012.61 09/10 14:55
5A 7B 0003.17 09/08 15:19	5A 7B 0006.34 09/09 15:15	5A 7B 0006.37 09/10 00:12	5A 7B 0012.63 09/10 13:55
4A 7B 0003.17 09/08 15:04	4A 7B 0006.35 09/09 14:45	4A 7B 0006.37 09/09 23:42	4A 7B 0012.65 09/10 12:55
3A 7B 0003.17 09/08 14:49	3A 7B 0006.36 09/09 14:15	3A 7B 0006.37 09/09 23:12	3A 7B 0012.68 09/10 11:55
2A 7B 0003.17 09/08 14:34	2A 7B 0006.37 09/09 13:45	2A 7B 0006.38 09/09 22:42	2A 7B 0012.70 09/10 10:55
1A 7B 0003.54 09/08 14:19	1A 7B 0032.07 09/09 13:15	1A 7B 0006.60 09/09 22:12	1A 7B 0012.95 09/10 09:55

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seal the Teflon spacers to the sampling cartridges while the other sampling head design utilized a bolt-type arrangement.

Pressure Tests

Pressure leak tests were conducted with both sampling head designs. The heads were sealed and a pressure source from a He tank reservoir was applied. In line was a flow meter and pressure gauge for monitoring leaks. A 10 psi pressure was applied and then turned off from the source, the ability to hold the applied pressure was monitored on the pressure gauge.

Both types of heads (screw-cap and bolt-type) were found to leak profusely in these initial tests. Table 77 gives this leakage rate. The leakage in both cases was attributed to the noncompressability of the Teflon® spacer between the block and end-plates. Eventhough the bolt-on end plate could be tightly secured, warping of the end-plate aggravated the leakage problem.

Thus the Teflon® spacers were omitted at both ends of the sampling head, permitting the Viton o-rings (size 114-Ace Lab Glass and size 010-Cajon) to seal around each end of the sampling cartridge and the end plate. Pressure leak tests to 10 psi with He revealed no leaks on the bolt type and screw-cap heads. A helium leak detector set at "high" sensitivity was used to monitor around all fittings.

Background of Stored Tenax® GC Cartridges

The initial background studies began with determining whether clean Tenax cartridges placed in the sampling head could be maintained background free during periods of storage. The initial experiment employed 24 hr storage and then subsequent experiments were 45 and 95 hrs long.

Tenax cartridges examined throughout the storage study were subjected to TD/HRGC analysis with the integration of the background area using a CDS 111 Varian Chromatography Data System. The chromatographic parameters used in the storage study are given in Table 78.

Table 79 presents the results obtained for the background level for Tenax cartridges stored in the prototype sampling heads. In general, the background increased above that observed for a cartridge stored for the same period of time in a Kimax® culture tube. Best results were obtained with the phenolic screw-cap utilizing Teflon O-rings for a storage period of 41 hours.

Table 77. INITIAL LEAK TEST RESULTS

Sampler Head Type	Delivered Pressure[a] (psi)	Final Pressure[b] (psi)	Leak Rate[c] (L/min)
Screw-cap	10	2	3
Bolt-on	10	2	2.5

[a] Measured by regulator at tank source.

[b] Measured by in-line pressure gauge.

[c] Measured by in-line rotameter, max. initial rate achieved.

Table 78. CHROMATOGRAPHIC PARAMETERS USED IN STORAGE STUDY

Parameter	Conditions
Column Temperature	40°C (2 min) $\xrightarrow{4°C/min}$ 210°C (2 min)
Capillary	SE-30 WCOT/$BaCO_3$; 85 m
Injector Temperature	220°C
Detector Temperature	270°C
Attenuation (AUFS)	X64, 10^{-11}
GC	Varian 3700
Data System	CDS-111

Table 79. BACKGROUND LEVEL STUDY FOR TENAX® GC CARTRIDGES STORED IN PROTOTYPE SAMPLING HEADS USED FOR THE AUTOMATIC SAMPLER

	Bolt Type/ Teflon O-Rings		Screw Cap/ Teflon O-Rings		Screw Cap/ Viton O-Rings
Storage:	45 hr	91 hr	45 hr	95 hr	42 hr
Initial Control[a]	6.21	6.43	17.96	2.62	1.87
Final Control[b]	5.82	6.17	15.10	1.83	2.74
Sample[c]: Mean	28.42	68.09	27.35	108.55	56.26
S.D.	9.68	18.73	6.48	13.81	18.43
C.V.	34.06	27.52	23.69	12.73	32.75

[a] Area counts of cartridge background determined immediately after preparation.

[b] Area counts of cartridge background stored in Kimax® culture tube sample period of time as "sample".

[c] Cartridge stored in sampling head of automatic sampler, mean of 3 determinations.

Additional research was conducted to determine the merits of a screw-cap vs. bolted head for sealing cartridges. Cleaned and vacuum pumped Viton O-rings were used. The background study was conducted over a 2 week period. The results in Table 80 clearly indicates the ineffective sealing using the screw-cap type closure. Bolt-on end plates preserved the sampling cartridges as well as culture tubes.

With the subsequent omission of Teflon® spacers in the sampling heads (see above) the background on Tenax GC cartridges was further investigated. All components were cleaned as follows. The sampling heads and end plates were washed twice in methanol (B&J) and once in pentane (B&J), air dired and then placed in a vacuum oven for 2-4 h at 110°C. Viton o-rings washed in warm Isoclean® solution with sonication for 1 min, rinsed 3-6 times with warm water and sonicated for 1 min, 3 times in distilled water, air dired and placed in a vacuum oven for 2-4 h at 40°C.

Tenax® GC cartridges were prepared as previously described (Section 6) using glass tubes designed to fit the sampling head.

Storage experiments were conducted using both sampling head designs. The background on each cartridge was determined by TD/HRGC as previously described, with the area integrated under all the peaks occuring in the chromatogram for a specified time. These results are given in Table 81. These data indicate that the Tenax cartridges stored in the bolt-type head was similar to culture tube storage. However, when each cartridge was removed from the sampling head, the remaining cartridges were potentially exposed to atmospheric background thus confounding the subsequent results. The storage experiment was repeated, but the heads were opened only once, 7 days after storage. These results are given in Table 82.

All of the experimental data indicates that the bolt-type sampling head is a better design and thus it was incorporated into the automatic sampler.

Table 80. BACKGROUND LEVELS OF TENAX CARTRIDGES STORED IN SAMPLING HEADS COMPARED TO CARTRIDGES STORED IN CULTURE TUBES

Storage Vessel	Slope[a]	Correlation Coefficient
Culture tubes	69	0.744
Sample head with bolt-on end caps	77	0.672
Sample head with screw-on end caps	790	0.936

[a] Based on $y = mx + b$ where y is the total instrumental response, and x is the time in days of storage. Therefore, the greater the slope, the greater the level of contamination over time.

Table 81. BACKGROUND OF TENAX® GC CARTRIDGES STORED IN SAMPLING HEADS

Storage Mode	Storage Time (days)	Area[a] (Arbitrary Units)
Culture tubes	0	0
	2	0
	7	3,823
	14	862 ± 182
Bolt-type head	0	0
	2	1,696
	7	1,772
	14	1,288 ± 162
Screw-cap head	0	0
	2	3,397
	7	4,593
	14	14,732
	15	10,128

[a] Area was summed for all chromatographic peaks occurring in the 62 min of the run.

Table 82. BACKGROUND OF TENAX® GC CARTRIDGES STORED IN BOLT-TYPE SAMPLING HEAD

Storage Mode	Storage Time (days)	Area[a] (Arbitrary Units)
Culture tubes	0	0
	7	758 ± 191
Bolt-on Type Head	0	0
	7	1,856 ± 924

[a] Area was summed for all chromatographic peaks occurring during the first 12 min of the run.

SECTION 10

PRELIMINARY DEVELOPMENT OF DIFFUSION TUBES FOR LOW VAPOR-PRESSURE COMPOUNDS

INTRODUCTION

In addition to the preparation of permeation tubes for selected test compounds, a parallel effort included an investigation into a method for synthesizing a flowing stream of air/vapor mixture of low vapor pressure organics (b.p. > 215°C). There is no literature report for accomplishing this.

DELINEATION OF A DIFFUSION TUBE SYSTEM

Chromatographic Method

A new approach was devised and tested for delivering constant levels of polar and/or non-volatile compounds for the purpose of synthesizing air/vapor mixtures. This method employed the use of vessels containing the organic compound to which was attached a short chromatographic column (Fig. 86). The concept examined was the use of a GC phase coated onto a support to give controlled diffusion of vapor from the vessel when the container and chromatographic column are maintained at a constant temperature. The selection of the GC phases were based upon the McReynold's No. and the polarity of diffusing compound. Thus the rate of diffusion is controlled by temperature, phase loading, and length of chromatographic column. A model system which would allow the control on a rate of diffusion to within a factor of 5 for a group of model compounds with vapor pressures that are significantly apart was desired.

To test this system diffusion tubes for those compounds listed in Table 83 were prepared. For some compounds permeation tubes have been successfully prepared; however, they served as cross-checks.

A series of chromatographic supports (Chromosorb-W, HP) coated with varying percents of OV-17 (1,3,5 and 10%) in chromatographic columns of varying dimensions (1.25 mm, 2.5 mm i.d.) and packing bed depths of various

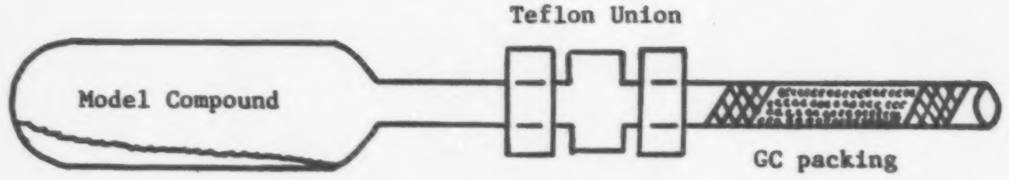

Teflon Union
Model Compound
GC packing

Figure 86. Schematic of diffusion tube and GC column.

Table 83. COMPOUNDS EXAMINED IN MODIFIED DIFFUSION TUBES

Compound	GC Packing	Column Dimensions i.d. x length (mm) (bed)
Pyridine	OV-225	2.0 x 6.0
Phenol	OV-225	2.0 x 6.0
Naphthalene	OV-17	2.0 x 6.0
Anthracene	OV-17	2.0 x 2.0
Quinoline	OV-17	2.0 x 3.0
1-Naphthylamine	OV-225	2.0 x 2.0
1,2-Dihydroxybenzene	OV-225	2.0 x 3.0
N-Nitrosodiethylamine	DEGS	2.0 x 6.0

lengths (0.5, 1.0 and 3.0 cm) was prepared and attached to a reservoir of pyridine and phenol. The reservoir with the chromatographic column was placed in an oven bath at 70 and 80°C with the exit of chromatographic column attached to a manifold through which nitrogen gas was passed. An injection port downstream of the manifold served for the withdrawal of a gas aliquot for analysis by GC/FID to determine the concentration of pyridine and phenol in the synthesized air/vapor mixture.

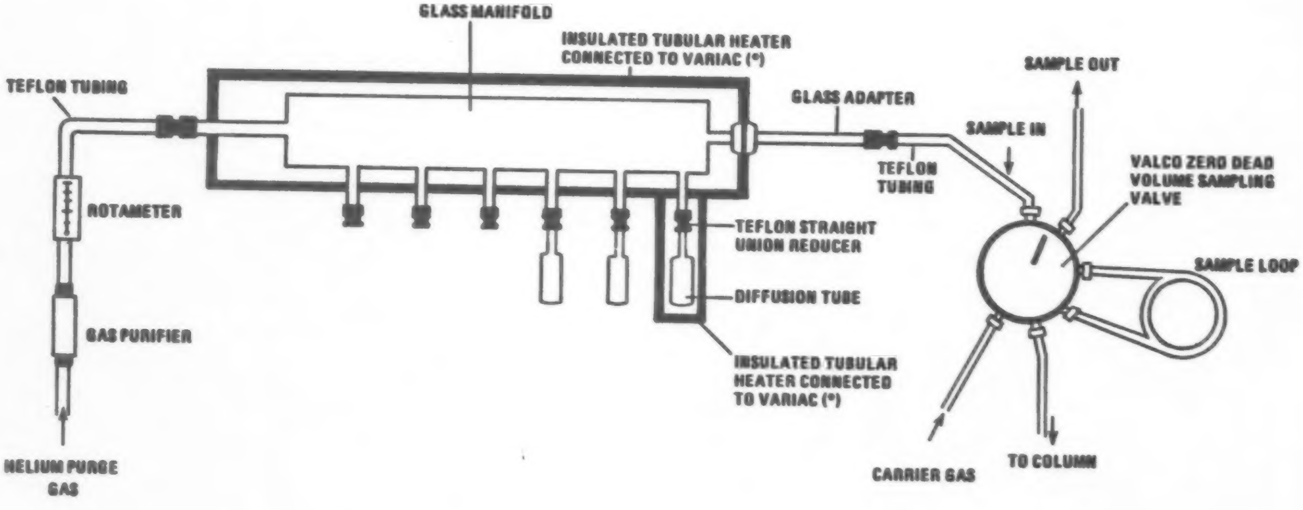
Examining the various variables of length, packing and phase loading, the results indicated that some control on diffusion could be achieved to generate different levels by selecting these parameters; however, a difference of within an order of magnitude could not be achieved. It was desired that the parameters would provide enough variability for model compounds of varying vapor pressures and that they could be made to diffuse near the same rates so that a synthetic air/vapor mixture might be synthesized as a multicomponent mixture at one particular bath temperature.

The encouraging aspect of this approach was the rather constant level of compound which was sparged into the nitrogen gas stream after equilibration had been achieved. The levels of the synthetic air/vapor mixture for pyridine and phenol appeared to be controllable to ±2% over several hours.

Gas-solid sorbents - Spherocarb, Tenax GC, Chromosorb 102, Porapak N and XAD 2 - were also evaluated. Modified diffusion tubes (pyridine and phenol) were placed in an oven bath at 80° with a 1.25 mm i.d. x 2.0 cm bed length of each of the sorbents which led to a manifold whereby the air/vapor mixture generated was examined by GC/FID. The equilibration to a constant level of pyridine vapor was examined *vs*. time for each of the solid sorbents. The maximum difference observed between Tenax® GC and Spherocarb was about a factor of 2. This difference was deemed unacceptable for the work in this project since the vapor pressures for the model compounds to be incorporated into such a method are greater than an order of magnitude. Thus, constant levels into a single synthetic air/vapor mixture stream were not possible with this approach.

Non-Chromatographic Method

Another modified diffusion tube system was assembled as shown in Figure 87. By equalizing the vapor pressures via selecting appropriate


GLASS MANIFOLD
INSULATED TUBULAR HEATER CONNECTED TO VARIAC (*)
TEFLON TUBING
GLASS ADAPTER
SAMPLE OUT
SAMPLE IN
TEFLON TUBING
VALCO ZERO DEAD VOLUME SAMPLING VALVE
SAMPLE LOOP
ROTAMETER
TEFLON STRAIGHT UNION REDUCER
DIFFUSION TUBE
GAS PURIFIER
INSULATED TUBULAR HEATER CONNECTED TO VARIAC (*)
HELIUM PURGE GAS
CARRIER GAS
TO COLUMN

(*) THERMO-COUPLES MONITOR TEMPERATURE (°C)

HEATING TAPE IS WRAPPED AROUND ALL TUBING IN THIS REGION TO AVOID COLD SPOTS (*)

Figure 87. Modified diffusion tube system for generating vapor/gas mixture.

temperatures on the diffusion tube, it was possible to deliver a constant and relatively equilivalent value of each of the test model compounds in question. The initial studies determined whether a constant level could be maintained for a synthetic air/vapor mixture over a relatively long period of time (8 hrs) in order to be useful for the evaluation of collection devices. By using a vapor pressure data and variable temperatures, the equilibration times and constancy of delivery as well as accuracy of the individual compounds were examined.

Initially a 1 mL sample loop was installed. However, broad chromatographic peaks resulted on the capillary column and a 150 μL sample loop and a 5 sec injection time was then employed and proved successful. A minor constructural modification was made to the diffusion tube system to eliminate back pressure. A union T was placed in line with the transfer line to the sampling loop to eliminate back pressure and the exhaust was connected to a charcoal trap. Flows from the exhausts of the loop and vent lines were measured with bubble devices to obtain total flow and calculated concentrations of air/vapor mixtures.

Using the system shown in Figure 87 the temperatures on the diffusion tubes were adjusted so than an equivalent amount of each compound was delivered into the gas stream to provide a synthetic gas/vapor mixture. This device will permit the replacement of a permeation system on the portable diluter when model compounds with very low vapor pressures are used for evaluating sampling devices.

The modified diffusion tube system was tested for its stability over 4 and 7 hour time periods. Peak heights were measured as the compounds were held at the same operating temperature during this entire period. No attempt to quantify the concentrations of the compounds by comparison with liquid injection was made; however, future studies should be conducted to establish equivalency.

Table 84 presents the results obtained for the stability of the diffusion tube system for naphthalene analyzed over a 4 hr period. Indicated are the operating parameters and the mean standard deviation and coefficient variation of the peak height for this compound. Likewise, a 7 hr stability study for naphthalene, quinoline and o-chloronitrobenzene was also conducted and these

Table 84. DIFFUSION TUBE STABILITY FOR NAPHTHALENE - 4 HOUR STUDY

Parameter	Set Point
Diffusion tube Temp.	200°C ± 1°C
Manifold Temp.	200°C
Transfer line Temp.	200°C
Valve Temp.	270°C
Manifold flow	1.0 L/min
Injection period	10 sec
Injection volume	150 µL
Detector Temp.	300°C
Column Temp.	160°C
Column	Carbowax CP-Wax 20 (50 m x 0.5 mm I.D.)
Capillary flow	3.4 mL/min

Results

Mean	131.2 mm (peak height)[a]
S.D.	6.5 mm
% S.D.	4.9

[a] Represents 48 data points.

results are shown in Table 85. In general the stability, i.e. the variation as expressed by the percent relative standard deviation was small for the time period investigated which implies that this technique may be suitable for the synthesis of air/vapor mixtures of the group of compounds which cannot be prepared in permeation tubes.

Table 85. DIFFUSION TUBE STABILITY FOR NAPHTHALENE, QUINOLINE, o-CHLORONITROBENZENE - 7 HOUR STUDY

Parameter		Set Point
Diffusion tube Temp.		
	Naphthalene	99°C
	Quinoline	154°C
	o-Chloronitrobenzene	166°C
Manifold Temp.		200°C
Transfer line		210°C
Valve Temp.		270°C
Sample Volume		150 μL
Injection Time		5 sec
Sample Loop Flow		24 mL/min
Tee Flow		3,505 mL/min
Total Flow		3,529 mL/min
Detector		300°C
Column		190°C
Capillary Flow		3.4 mL/min

Results

	Mean ± S.D. (C.V.)[a]
Naphthalene	120.9 ± 7.0 (5.8)
Quinoline	92.9 ± 5.1 (5.4)
o-Chloronitrobenzene	99.9 ± 9.9 (9.9)

[a] Represents 42 data points.

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